Organic Thio-Compounds

with special reference to

Tautomeric Changes and the Formation of Polysulphonium Derivatives

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Part I

By

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PREFACE

The Governing Body of the College of Science has expressed a desire that the researches undertaken in the various departments should be published from time to time in the shape of memoirs or bulletins ; hence the present publication. Time alone can show whether there will be a continuity in the regular issue of such memoirs.

Some of the papers in the present volume have already appeared in a more or less condensed form in the Journal of the Chemical Society of London. They have been reproduced with additional matter so as to form a connecting link in the chain of organic thio-compounds giving rise to tautomeric changes and the formation of polysulphonium derivatives.

The difficulties and hardships which beset the path of those young aspirants who would follow a scientific career in this country are manifold. Hitherto, law, medicine, engineering and the civil services have naturally attracted the best intellects, as science has but little to offer to her devotees. I can only repeat here, what I have said elsewhere, namely "that those who pursue Chemistry in India at the present state of its progress must not expect to reap immediate benefit in the shape of rich pecuniary rewards. To a sincere and devoted student, the pursuit of knowledge for its own sake always carries its rewards. A man of science is a member of a privileged class—to him has been committed the sacred task of unravelling the mysteries and secrets of nature. Attracted by the glamour of a material civilisation we hope we shall not forget our noble heritage of plain living and high thinking."* Again :

"If we read carefully the history of the different branches of science we invariably find that they have attracted votaries in the early stages of their progress in the midst of almost insuperable difficulties. You all know that Copernicus held back the publication of his great book "On the Revolutions of the Heavenly Bodies" for 36 years for fear of giving offence to the all-powerful Church ; that Bruno was burned at the stake for teaching the plurality of worlds, and Galileo visited with the terrors of the Inquisition for his vindication of the Copernican doctrine. Nay, Roger Bacon, one of the precursors of our own science, was thrown into prison and had to rot in a dingy cell of a cloister at Oxford for practising the Black Art, as chemistry was then called. Browning in his "Paracelsus" has delineated the wrestlings and inward longings of an ideal alchemist, who is only an honest seeker-after-truth, who pursues knowledge for its own sake irrespective of what it brings. Voltaire tells us that at the time of Newton's death there were not 20 readers of Principia out of Britain. These great and mighty interpreters of the laws of nature cared not for name or fame, but considered themselves lucky if only they could be instrumental in giving to the world the results of their lifelong labours. Kepler had imposed upon himself years of incessant toil including midnight vigils in observing and recording the motions of heavenly bodies; and after embodying the results of his labours he exclaims, "I may well wait a hundred years for a reader, since God Almighty has waited six thousand years for an observer like myself."

---

* "Progress of Chemistry in Bengal."

If Europe is what she is to-day—if she is in the van of scientific progress—it is in no small measure due to the self-denying ordinances of these great heroes in science and their worthy successors.

I have been led to indulge in this digression because without a brief historical retrospect of the development of sciences in Europe much of what I am going to say will not be properly understood.

Those who intend to pursue chemistry in India must not expect to reap a rich harvest in the immediate or near future. India has been a *tabula rasa* so far as the cultivation of physical sciences is concerned for the last 1,000 years or perhaps more. In Germany or in England for the last 300 years—*i. e.*, from the time of Paracelsus and Basil Valentine and Newton and Boyle the lamp has been burning dimly in the early stages, but more and more brilliantly in the 18th and 19th centuries. We in the East, on the other hand, have been living in silent and ecstatic meditation. To the Hindu the material world is but an illusion and Sankara as an exponent of the Vedanta Philosophy is unsparing in his criticism and denunciation of the atomic theory as propounded in the Vaiseshika philosophy, ridiculing the author of the system itself as 'Kanada' or atom-eater. No wonder M. Cousin in his "History of Philosophy" in giving an analysis of the Yoga philosophy and the Bhagavat-Gita, which he calls a monument of the greatest price, quotes such passages as these: "Science is superior to practice, and contemplation is superior to Science; prefer contemplation to Sceince, inaction to action, faith to work, etc." and concludes by observing that as man despising himself has not been able to take any thought for recalling the memory of his actions there is no history of man, and no chronology in India. No wonder Mill should write: "The Hindu boys display marvellous precocity in appreciating a metaphysical proposition which would hopelessly puzzle an English lad."

"Remember, gentlemen, what the transplantation of western sciences in such a land and amidst such environments means. Those who are pioneers in this field have no traditions to go by or follow up; they have to chalk out their own path and formulate their own schemes and carry them out as best as they may. Difficulties arise at every turn but with faltering steps the weary pilgrim must keep marching on towards the goal; happy if he reaches it but equally happy if he perishes in the attempt."*

In my "History of Hindu Chemistry" I have devoted a chapter to the discussion of some of the causes which brought about the decline of scientific spirit in India, and helped to usher in a period of intellectual stagnation; we hope we have slept off the torpor ages and that it will be ours once more to extend the bounds of knowledge.

The sand is running down fast in the hour-glass of my life. The work already turned out by some of our pupils is full of hopeful augury for the future. I am grateful that it has been vouchsafed unto me to get a Pisgah view of the promised land.

---

* "Pursuit of Chemistry in Bengal"—Calcutta University Extension Lecture, 1916.

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Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides.

Part IV

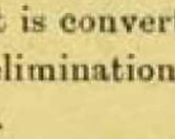
Chain Compounds of Sulphur—*continued.*

BY

Prafulla Chandra Rây and Prafulla Chandra Guha.

In the previous communication of the present series (Pt. III. Trans. Chem. Soc. 1917, *111*, 101) it has been shown that whenever a potential mercaptan (*e.g.* thioacetamide, thiobenzamide, thiourea *etc.*), is treated with mercuric nitrite, the radical (—$SHgNO_2$) as a rule, gets detached and assumes the stable form $[3(SHgNO_2)\,HgO]_2$, whilst the organic component is converted into an aldehyde as also the corresponding acid with elimination of ammonia or substituted ammonia as the case may be.

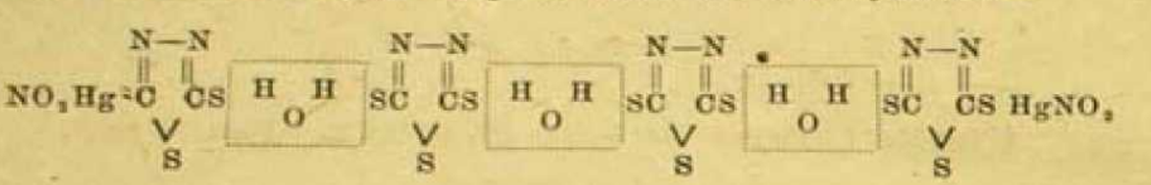
In the present investigation the reactions of a large number of actual and potential mercaptans as also of dimercaptans, some of them belonging to the cyclo-group, have been studied. It was expected that in these the molecules being of a more complex nature, the radical specially (-$SHgNO_2$), would far more readily part company with the parent substance and lead an independent existence in the shape of $[3(SHgNO_2)HgO]$. The result has proved to be just the reverse. Mercurimercaptide nitrites of the ali-and heterocyclic compounds have been found to be stable compounds. A few typical cases will make the point clear. Phenyldithiobiazoline sulphydrate,



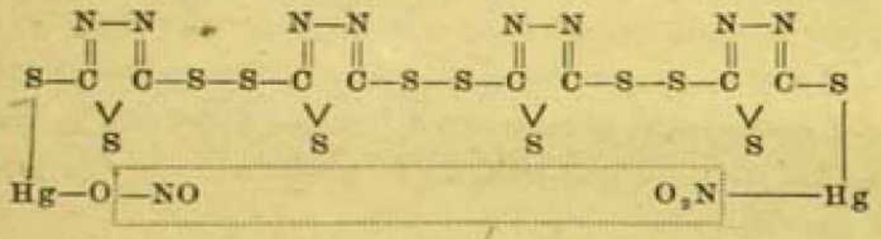
yields with mercuric nitrite the corresponding mercaptide nitrite, the reaction being of the ordinary type;

$$RS\boxed{H+NO_2}Hg\,NO_2 = RSHgNO_2 + HNO_2$$ (Cf. Trans. Chem. Soc. 1916, *109*, 131).

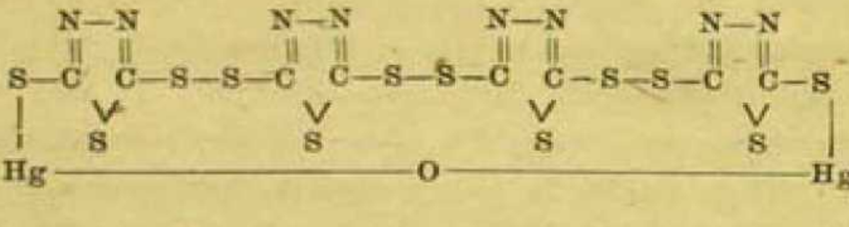
When a dimercaptan like thiobiazole-disulphydrate is similarly treated the reaction follows indentical lines but owing to the ready oxidisability of this class of compounds, it advances a step further, giving rise to a remarkable series of compounds containing sometimes as many as six or even eight sulphur atoms in a chain, thus :—



What happens is that often four molecules simultaneously take part in the reaction, the extreme members are converted into mercaptide nitrites and the nitrous acid set free reacts in turn upon the remaining (SH) groups, reproducing the following compound, which, it will be readily seen, is a tetradisulphide-dimercaptide-dinitrite :—

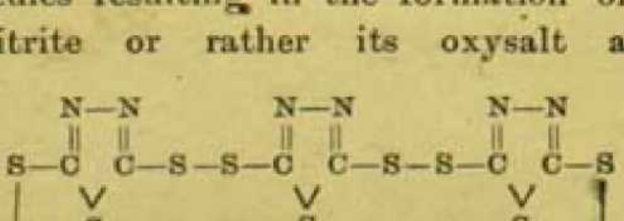


or

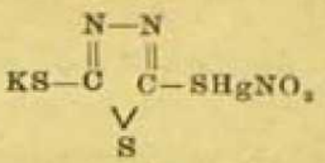


But as the molecule is a very heavy one it cannot retain the load of two (NO_2)'s; N_2O_3 (*i.e.*, $NO_2 + NO$) is evolved and an oxy compound is ultimately formed (Cf. Trans. Chem. Soc. 1916, *109*, 133).

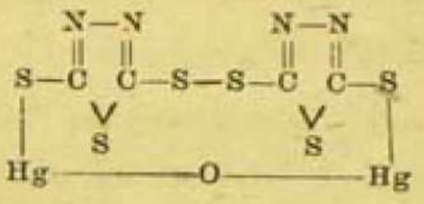
Sometimes, the oxidation does not go so far and is limited to only three molecules resulting in the formation of a tridisulphide-dimercaptide-dinitrite or rather its oxysalt as shown above,



It was reasonably expected that if instead of the dimercaptan itself, its potassium salt were substituted the corresponding nitrite-mercaptide would be formed, as, in this case, in place of nitrous acid its potassium salt would be generated and thus the chances of condensation of two or more molecules would be eliminated. This expectation has been realised. A compound of the formula



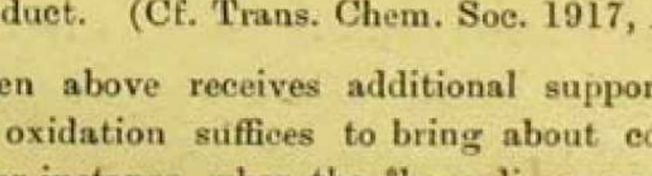
has been isolated. As the potassium-dimercaptide in aqueous solution undergoes partial hydrolysis reproducing the original mercaptan itself, it has also been found that when on keeping it for sometime it is acted upon by mercuric nitrite a compound of the formula



is formed. In this instance, as the nitrous acid available for oxidation is necessarily limited in quantity, a condensation of only two molecules takes place. It is noteworthy that when one molecule takes part in the reaction as in the previous case a real nitrite-mercaptide is formed, but only one-$HgNO_2$ group is fixed.

Whenever, however, two, three, or four molecules coalesce into a complex one the latter acquires the capacity to attach to the extreme ends of the chain two $-HgNO_2$ radicals; but as the heavily laden molecule has to part with a molecule of N_2O_3, an oxy-mercuri-salt is the ultimate product. (Cf. Trans. Chem. Soc. 1917, ***111***, 104).

The view taken above receives additional support from the fact that even aërial oxidation suffices to bring about condensation of three molecules; for instance, when the above di-mercaptan is treated with mercuric chloride, a mercaptide chloride of the formula



is formed and has been, in fact, actually isolated. It is thus evident that nitrous acid is by no means essential for the formation of the above chain compounds.

No less interesting is the behaviour of mercuric-nitrite towards thiophenol, which, as is well known, readily undergoes aërial oxidation and passes on to the stable disulphide form, Ph_2S_2. Besides the expected $PhSHgNO_2$, a remarkable compound, Ph_2S_3Hg, is obtained and sometimes another oxysalt corresponding to the empirical formula, $[3(PhS), HgO]_2$. It is only in exceptional cases (vide "Experimental" p. 13) that the expected nitrite mercaptide, $PhSHgNO_2$ is obtained but only in an impure form.

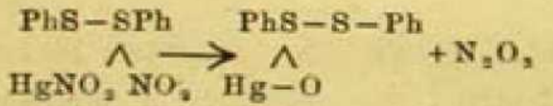
The reaction would seem to take place in the following stages :—

$$PhSH + NO_2HgNO_2 = PhSHgNO_2 + HNO_2 \quad \ldots \quad (1)$$

The nitrous acid thus liberated oxidises another pair of molecules of PhSH into diphenyldisulphide.

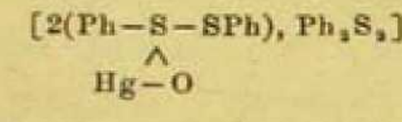
$$PhSH + O + HSPh = Ph-S-S-Ph + H_2O$$

The latter compound now forms the following compound with mercuric nitrite :—



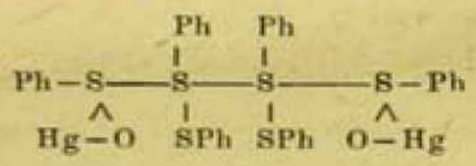
$$\underset{\substack{\wedge\\ \mathrm{HgNO_2,\ NO_2}}}{\mathrm{PhS-SPh}} \longrightarrow \underset{\substack{\wedge\\ \mathrm{Hg-O}}}{\mathrm{PhS-S-Ph}} + N_2O_3 \quad \ldots \quad \ldots \quad (2)$$

Two molecules of this compound again combine with a molecule of Ph_2S_2 (itself the product of oxidation of PhSH as stated above) and give rise to the compound,



$$[2(\underset{\substack{\wedge\\ \mathrm{Hg-O}}}{\mathrm{Ph-S-SPh}}), Ph_2S_2]$$

It may also be formulated as an "atomic" compound,

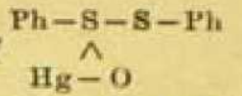
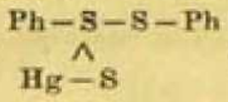


$$\begin{array}{ccccccc} & & \mathrm{Ph} & & \mathrm{Ph} & & \\ & & | & & | & & \\ \mathrm{Ph-S} & — & \mathrm{S} & — & \mathrm{S} & — & \mathrm{S-Ph} \\ \wedge & & | & & | & & \wedge \\ \mathrm{Hg-O} & & \mathrm{SPh} & & \mathrm{SPh} & & \mathrm{O-Hg} \end{array}$$

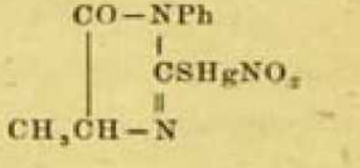
in which four sulphur atoms are tetravalent and two only divalent.

It may be objected here that as the compound $[3(PhS)HgO]_2$ is found to be free from phenyl-mercaptide-nitrite, the reaction as given above does not occur. It is, however, important to bear in mind that only the presence of a trace of nitrous acid is necessary to start the reaction; when once it is set a-going there will always be sufficient quantities of it available, according to the reaction in stage (2). In fact, it is inconceivable that mercuric nitrite should act upon a mercaptan without giving rise simultaneously to a nitrite-mercaptide and nitrous acid.

The compound represented by the empirical formula Ph_2S_3Hg, is evidently a mercaptide and the mechanism of the reaction involved in its formation does not seem to offer a ready solution. The simplest explanation would appear to be as follows :—

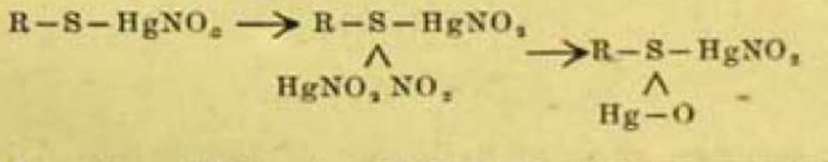
The oxygen atom of  $\overset{Ph-S-S-Ph}{\underset{Hg-O}{\wedge}}$ (see above) goes to oxidise two molecules of PhSH into PhSSPh. An atom of sulphur is now snatched away from the disulphide, which takes the place of oxygen producing  $\overset{Ph-S-S-Ph}{\underset{Hg-S}{\wedge}}$ and the monosulphide Ph—S—Ph. It is the strong affinity of mercury for sulphur which supplies the motive of the reaction. (Cf. conversion of thiocarbamide into cyanamide by means of mercuric oxide).

Another mercaptan belonging to the heterocyclic series, viz., phenyl-methyl-thiohydantoin, gave the nitrite-mercaptide conforming to the formula



$$\begin{array}{l} CO-NPh \\ \quad\;\; | \qquad | \\ \quad\;\; | \quad\; CSHgNO_2 \\ \quad\;\; | \qquad \| \\ CH_3CH-N \end{array}$$

It is now generally admitted that it is a real mercaptan (*i.e.* ψ or pseudohydantoin) and not a hydantoin and this is further confirmed by the fact that by the interaction of mercuric nitrite no break-up of the complex molecule occurs, neither does the divalent sulphur become tetravalent by taking on (—$HgNO_2$) and (—NO_2) thus :—

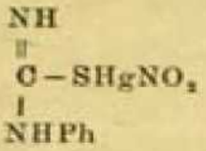


$$R-S-HgNO_2 \longrightarrow \overset{R-S-HgNO_2}{\underset{HgNO_2\ NO_2}{\wedge}} \longrightarrow \overset{R-S-HgNO_2}{\underset{Hg-O}{\wedge}}$$

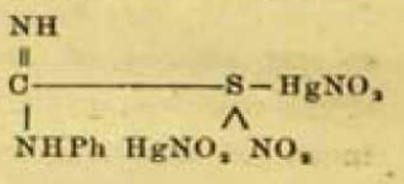
It has been invariably found that whenever a *potential* mercaptan is similarly treated, the reaction takes place, as indicated below.

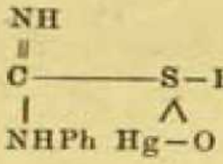
POTENTIAL MERCAPTANS.

The designation of potential mercaptans has been given to those thio-compounds which by withdrawal of an atom of hydrogen from the neighbouring NH_2 or NH group behave as mercaptans. The interaction of mercuric nitrite with thiocarbamide as also its alkylated derivatives, thio-acetamide and thio-benzamide, has already been studied. The investigation has now been further extended to the behaviour of this reagent towards the aryl substituted thiocarbamides, thiosemicarbazides, sulphocarbazides, etc. It has been found that the reaction follows the ordinary course, but no detachment of the organic radical takes place. Thus phenyl-thiocarbamide at first gives rise to :—

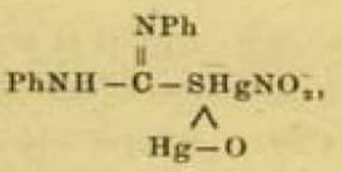


$$\begin{array}{l}\text{NH}\\ \|\\ \text{C}-\text{SHgNO}_2\\ |\\ \text{NHPh}\end{array}$$

The divalent sulphur atom at once takes up an additional molecule of $Hg(NO_2)_2$ and becomes tetravalent :  $\begin{array}{lll}\text{NH} & & \\ \| & & \\ \text{C} & \text{———————} & \text{S}-\text{HgNO}_2\\ | & & \wedge\\ \text{NHPh} & & \text{HgNO}_2\ \ \text{NO}_2\end{array}$

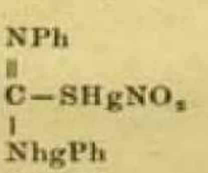
and ultimately the compound  $\begin{array}{lll}\text{NH} & & \\ \| & & \\ \text{C} & \text{————} & \text{S}-\text{HgNO}_2\\ | & & \wedge\\ \text{NHPh} & & \text{Hg}-\text{O}\end{array}$ is formed, with elimination of N_2O_3.

Sym. diphenyl thiourea or thiocarbanilide gives only on rare occasions the expected compound



$$\begin{array}{l}\qquad\quad\ \ \text{NPh}\\ \qquad\qquad \|\\ \text{PhNH}-\text{C}-\text{SHgNO}_2,\\ \qquad\qquad\quad \wedge\\ \qquad\qquad \text{Hg}-\text{O}\end{array}$$

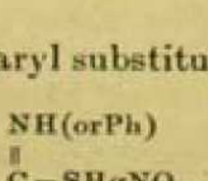
but the one which is generally obtained, conforms to the formula



$$\begin{array}{l}\text{NPh}\\ \|\\ \text{C}-\text{SHgNO}_2\\ |\\ \text{NhgPh}\end{array}$$

in the latter case, an atom of hydrogen of the adjacent imino-group is further replaced by (hg).

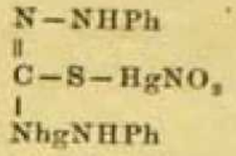
Thiosemicarbazide and its aryl substituted derivatives similarly yield



$$\begin{array}{l}\text{NH(orPh)}\\ \|\\ \text{C}-\text{SHgNO}_2\\ |\\ \text{NhgNH}_2\end{array}$$

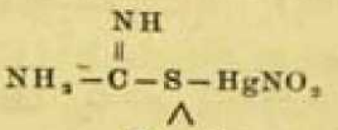
with the simultaneous displacement of an H atom of $NHNH_2$ by hg (Cf. guanidine in which two atoms of H are replaced by hg).

Diphenylsulphocarbazide also behaves similarly and gives the compound,



$$\begin{array}{l}\mathrm{N-NHPh}\\ \|\\ \mathrm{C-S-HgNO_2}\\ |\\ \mathrm{NhgNHPh}\end{array}$$

It is noteworthy, that as the molecules have already become highly loaded by the introduction of an additional (hg), the sulphur atom has lost the capacity of becoming tetravalent by further taking up (—$HgNO_2$) and (—NO_2). In connection with this it is important to remember that although thiocarbamide, as a rule, gives rise to the inorganic mercuri-sulphoxy-nitrite $[3(SHg\,NO_2)HgO]_2$, under special conditions it can be made to yield the compound

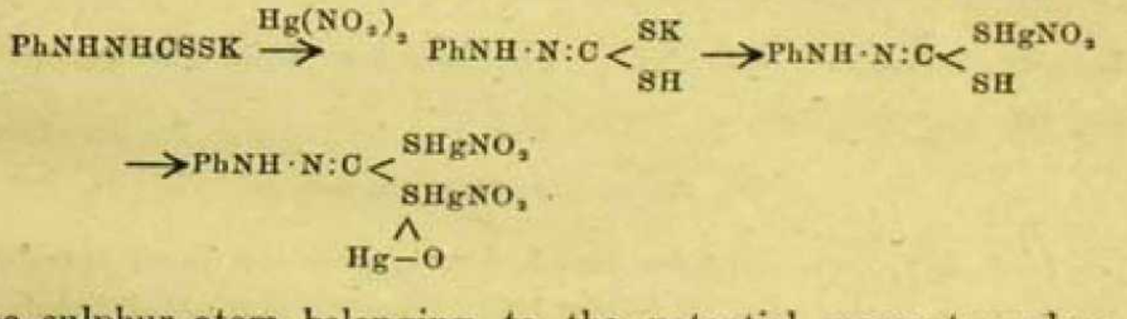


$$\begin{array}{c}\mathrm{NH}\\ \|\\ \mathrm{NH_2-C-S-HgNO_2}\\ \wedge\\ \mathrm{Hg-O}\end{array}$$

(l. c. p. 192). In other words, what was regarded as an exception or aberrant type of reaction, now becomes the rule.

Attention may also here be drawn to the interesting analogous case of phenyl dithiocarbazinic acid (or rather its K-salt), which combines in itself the function of a real as also a potential mercaptan.

Thus,



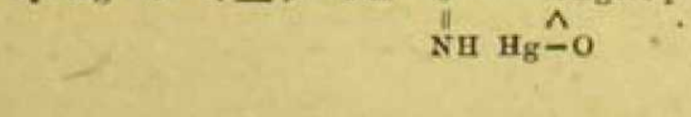
$$\mathrm{PhNHNHCSSK}\xrightarrow{\mathrm{Hg(NO_2)_2}}\mathrm{PhNH\cdot N{:}C}<\begin{array}{l}\mathrm{SK}\\ \mathrm{SH}\end{array}\longrightarrow\mathrm{PhNH\cdot N{:}C}<\begin{array}{l}\mathrm{SHgNO_2}\\ \mathrm{SH}\end{array}$$

$$\longrightarrow\mathrm{PhNH\cdot N{:}C}<\begin{array}{l}\mathrm{SHgNO_2}\\ \mathrm{SHgNO_2}\\ \;\wedge\\ \mathrm{Hg-O}\end{array}$$

The sulphur atom belonging to the potential mercaptan alone becomes tetravalent.

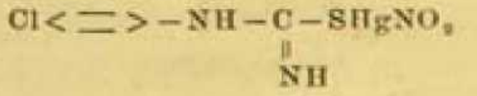
It thus verifies the law enunciated above inasmuch as the two sulphur atoms behave differently.

Perhaps one of the most striking reactions in the present series is that which takes place between mercuric nitrite and p-chlorophenylthiocarbamide. A nitrite free from chlorine of the empirical formula $C_7N_4H_6Hg_3S_2O_5$ is invariably obtained. Its constitution is evidently represented by the formula



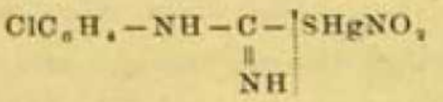
$$\begin{array}{l}\mathrm{O_2NHg-S-<\!=\!>-NH-\underset{\underset{\displaystyle NH}{\|}}{C}\text{———}\underset{\underset{\displaystyle Hg-O}{\wedge}}{SHgNO_2}}\end{array}$$

The mechanism of the reaction involved here is rather complicated. The first stage evidently gives,



$$\mathrm{Cl}<\!=\!>-\mathrm{NH}-\underset{\underset{\mathrm{NH}}{\|}}{\mathrm{C}}-\mathrm{SHgNO_2}$$

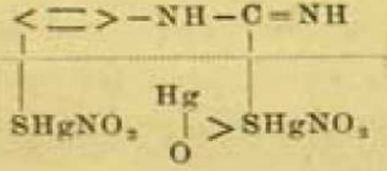
The chlorine in the altered condition of the molecule now becomes active and thus can no longer retain its place, and parts company with the parent body and in the nascent state acts upon a second molecule of the reaction product



$$\mathrm{ClC_6H_4}-\mathrm{NH}-\underset{\underset{\mathrm{NH}}{\|}}{\mathrm{C}}-\vdots\,\mathrm{SHgNO_2}$$

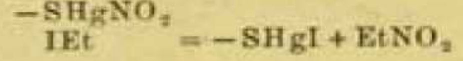
and brings about its disruption as indicated by the dotted line; while the stable radical ($-\mathrm{SHgNO_2}$) occupies the place of the halogen atom, the sulphur atom which is attached to the carbon atom of the thiocarbamide becomes tetravalent, as in the compounds described immediately above.

The constitution proposed is supported by the product it yields with ethyl iodide when the split takes place as indicated by the dotted line,



$$\begin{array}{l} <\!=\!>-\mathrm{NH}-\mathrm{C}=\mathrm{NH} \\ \;| \qquad\qquad\qquad\quad | \\ \mathrm{SHgNO_2} \quad \underset{\mathrm{O}}{\overset{\mathrm{Hg}}{|}}\!>\mathrm{SHgNO_2} \end{array}$$

Both the radicals ($-\mathrm{SHgNO_2}$) get detached from the parent body and the expected reaction takes place:—

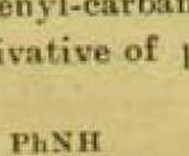


$$\begin{array}{l}-\mathrm{SHgNO_2}\\ \mathrm{IEt}\end{array} = -\mathrm{SHgI}+\mathrm{EtNO_2}$$

$(-\mathrm{SHgI})_2$, it will be remembered, is also the main product of the interaction between $[3\,(\mathrm{SHg\,NO_2})\,\mathrm{HgO}]_2$ and alkyl iodide. At the same time $[\mathrm{Et_2S_2}, \mathrm{HgI_2}, \mathrm{EtI}]$ is also formed (Cf. Trans. 1917, *111*, p. 108.)

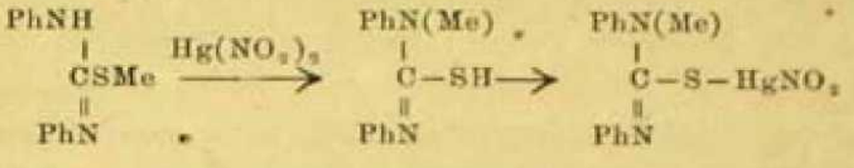
MIGRATION OF ALKYL RADICALS.

The behaviour of mercuric nitrite towards compounds of the type represented by Ph-imido-phenyl-carbamic-thiomethylester is equally striking. The latter is a derivative of pseudo (ψ) thiocarbamide and is assigned the formula



$$\begin{array}{l}\mathrm{PhNH}\\ \quad|\\ \quad\mathrm{CSMe}\\ \quad\|\\ \mathrm{PhN}\end{array}$$

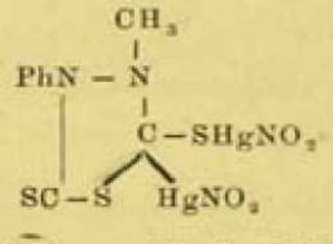
When it is treated with the reagent in question the original mercaptan is reproduced, the radical methyl being pushed back to the neighbouring nitrogen atom, hydrogen-taking its place, thus :—



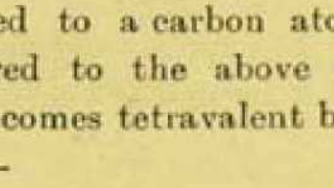
$$\begin{array}{c} PhNH \\ | \\ CSMe \\ \| \\ PhN \end{array} \xrightarrow{Hg(NO_2)_2} \begin{array}{c} PhN(Me) \\ | \\ C-SH \\ \| \\ PhN \end{array} \rightarrow \begin{array}{c} PhN(Me) \\ | \\ C-S-HgNO_2 \\ \| \\ PhN \end{array}$$

In fact nitrous fumes are evolved during the reaction. It is the marked affinity of the radical ($-HgNO_2$) for the sulphur atom which brings about the notable displacement of methyl radical. Additional instances will be furnished below (pp. 10—13).

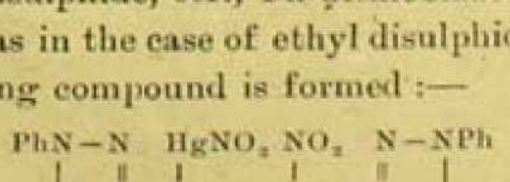
That the reactions described above are of wide applications are borne out by the deportment of methyl ether of phenyl dithiobiazoline sulphydrate. With mercuric-nitrite it gives the following compound :—



Here by the shifting of the radical (CH_3) to the neighbouring nitrogen atom, a bond of carbon indicated by the thick line is released and this is satisfied by an additional radical ($HgNO_2$). It might be objected that there is no instance as yet known in which ($HgNO_2$) group is directly attached to a carbon atom. Another alternative explaration might be offered to the above reaction, *viz.*, that the divalent sulphur atom becomes tetravalent by attaching to itself two ($HgNO_2$) groups, thus :—

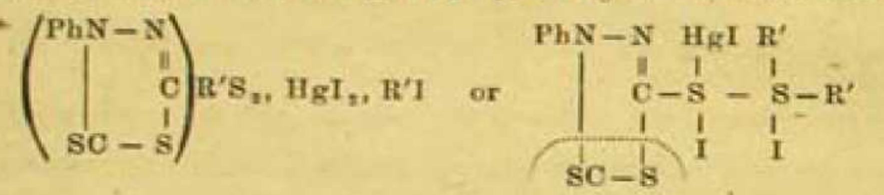


Last of all, may be described the behaviour of the above reagent towards a complex disulphide, *viz.*, Ph-dithiobiazoline disulphide. The reaction takes place as in the case of ethyl disulphide (Trans. 1916, *109* 133) and the following compound is formed :—

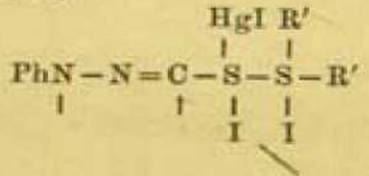


INTERACTION WITH THE ALKYL IODIDES:
FORMATION OF MONO, DI- AND TRI-SULPHONIUM COMPOUNDS.

The reaction follows the general course with this material difference that the complex radical being over-weighted can no longer retain its entity but the less durable part of it is usually shattered. Of special significance from this point of view is the rupture of the ring of the heterocyclic mercaptide nitrites. Let us take the specific case of dithiobiazoline derivative. When digested with an alkyl iodide we should expect [$RR'S_2$, HgI_2, $R'I$] *i.e.* in this case.

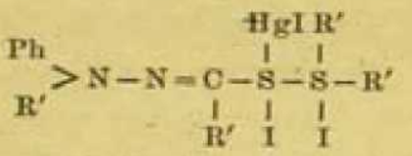


But a scission now takes place as shown by the dotted line and the disulphonium compound,



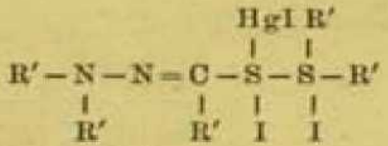
$$\mathrm{\underset{|}{PhN}-N=\underset{|}{C}-\overset{HgI}{\underset{I}{S}}-\overset{R'}{\underset{I}{S}}-R'}$$

is potentially formed, the unsaturated atoms C and N add on R′ from the interacting R′I and the product really formed is



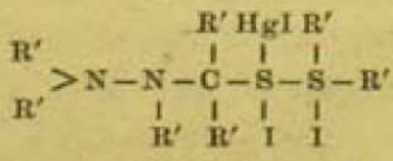
$$\begin{matrix}\mathrm{Ph}\\ \mathrm{R'}\end{matrix}\!>\mathrm{N-N=\underset{R'}{C}-\overset{HgI}{\underset{I}{S}}-\overset{R'}{\underset{I}{S}}-R'} \qquad \ldots \qquad \ldots \qquad \mathrm{(I)}$$

By further action of R′I the phenyl group is replaced by R′ and the following compound is formed :



$$\mathrm{R'-\underset{R'}{N}-N=\underset{R'}{C}-\overset{HgI}{\underset{I}{S}}-\overset{R'}{\underset{I}{S}}-R'} \qquad \ldots \qquad \ldots \qquad \mathrm{(II)}$$

Finally, the double bond between C and N is removed, two more R′'s being taken up and we get

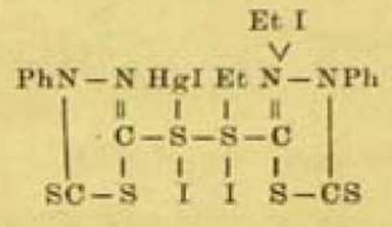


$$\begin{matrix}\mathrm{R'}\\ \mathrm{R'}\end{matrix}\!>\mathrm{N-\underset{R'}{N}-\overset{R'}{\underset{R'}{C}}-\overset{HgI}{\underset{I}{S}}-\overset{R'}{\underset{I}{S}}-R'} \qquad \ldots \qquad \ldots \qquad \mathrm{(III)}$$

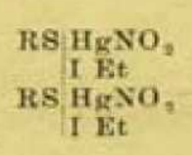
By the action of methyl iodide, two compounds corresponding to stages I and III have been isolated, whereas, in the case of ethyl iodide only one compound has been isolated which corresponds to stage II as shown above.

As a matter of fact, it has been observed that the yield of the compound with methyl iodide, corresponding to stage I decreases with the lengthening of the period of reaction. So, it is evident that it is only an intermediate product which is gradually transformed into the compounds corresponding to stages II and III, which undergo no further change.

It has already been shown that these disulphonium-mercuri-iodides can be directly synthesised from their components (l. c. 611). Dithiobiazoline-disulphide dissolved in carbon-disulphide was refluxed with ethyl iodide and mercuric iodide. In this case, not only was there no rupture of the dithiobiazoline radicals, but in one instance one of the tertiary nitrogen atoms became quaternary by taking up a molecule of ethyl iodide and the compound which was obtained corresponded to the formula :—



It is thus evident that the rupture of the complex radical can only take place when it separates out in the *nascent* state, and is therefore in a state of strain and is endowed with vibratory motion.

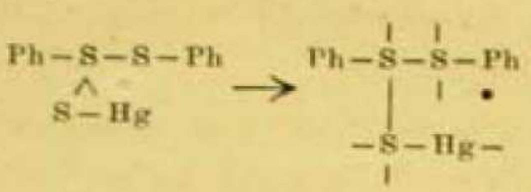


$$\begin{array}{l|l} RS & HgNO_2 \\ & I\ Et \\ RS & HgNO_2 \\ & I\ Et \end{array} \qquad \text{(l.c. 603)}$$

This is what might have been expected. In the ready made molecule the component radical is inert and sluggish and naturally does not lend itself to disruptive influences. On the other hand when dithio-biazoline-mercaptide-nitrite is treated with an alkyl iddide, it suffers a split and its stable portion alone takes part in the formation of the disulphonium compound.

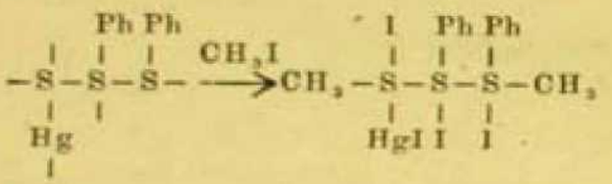
The reaction of alkyl iodides on phenyl-mercuri-mercaptide-nitrite follows the usual course and yields compounds of the general formula [$PhR'S_2$, HgI_2, $R'I$]. The compound obtained from Ph_2S_5Hg and alkyl iodide is what was actually anticipated. It contains all the sulphur atoms in a single chain and all of them are quadrivalent. The reaction can be explained in the following way :—

In the first stage the bond between Hg and S as shown by the dotted line is severed.



$$\begin{array}{c} Ph-S-S-Ph \\ \wedge \\ S-Hg \end{array} \longrightarrow \begin{array}{c} |\quad| \\ Ph-S-S-Ph \\ |\quad| \\ -S-Hg- \\ | \end{array}$$

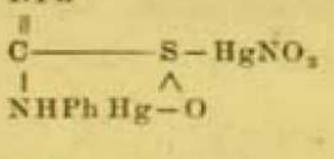
This assumed intermediate product in presence of an excess of alkyl iodide acquires the power of transforming all of its sulphur atoms into the quadrivalent form and the unsaturated bonds are simply saturated by the iodine atoms and alkyl groups,



$$\begin{array}{c} Ph\ \ Ph \\ |\quad|\quad| \\ -S-S-S- \\ |\quad| \\ Hg \\ | \end{array} \xrightarrow{CH_3I} \begin{array}{c} I\quad Ph\ \ Ph \\ |\quad|\quad| \\ CH_3-S-S-S-CH_3 \\ |\quad|\quad| \\ HgI\ \ I\quad I \end{array}$$

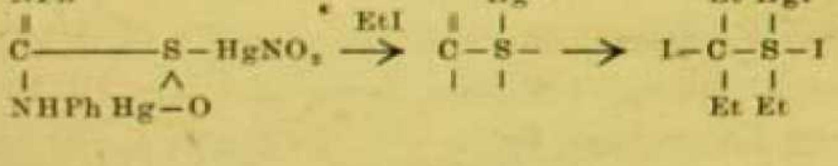
and thus a *trisulphonium* compound is formed.

An interesting monosulphonium compound has been obtained from the mercaptide nitrite of thiocarbanilide, *viz.*,



$$\begin{array}{l} NPh \\ \| \\ C\text{———}S-HgNO_3 \\ |\qquad\quad \wedge \\ NHPh\ Hg-O \end{array}$$

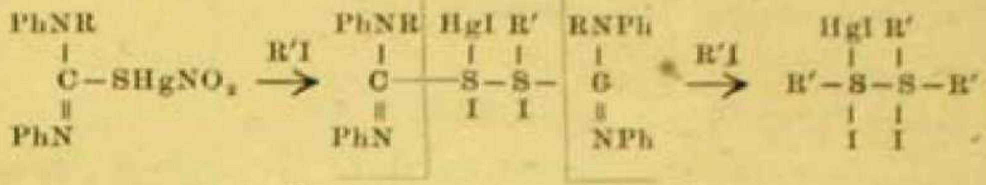
in which the sulphur atom is already tetravalent. It cannot and in fact does not show any tendency to give a disulphonium compound by doubling the formula (or rather by doubling the sulphur chain). The reaction probably takes place as shown below :—



$$\begin{array}{l} NPh \\ \| \\ C\text{———}S-HgNO_3 \\ |\qquad\quad \wedge \\ NHPh\ Hg-O \end{array} \xrightarrow{EtI} \begin{array}{c} \quad Hg- \\ \|\quad | \\ C-S- \\ |\quad | \end{array} \longrightarrow \begin{array}{c} Et\ HgI \\ |\quad | \\ I-C-S-I \\ |\quad | \\ Et\ \ Et \end{array}$$

Here both the phenylamino-groups are replaced by ethyl.

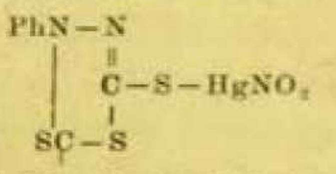
The interaction of mercaptide-nitrite of phenyl-imidophenyl-carbamic-thio-alkylesters with alkyl iodide takes place as in the case of the simple mercaptide nitrites forming compounds of the type $[R_2S_2, HgI_2, R'I,]$ and in fact the reaction advances a step further, both of the complex groups being replaced by simple alkyl ones.



It may be added here in this connection that the formation of this type of disulphonium compounds proves conclusively the hypothesis of pushing back (migration) of alkyl groups to the adjacent amino- or imino-groups in the formation of the mercaptide nitrites; the (—$HgNO_2$) groups remain attached to the sulphur and not to the neighbouring nitrogen (vide *ante* p 8). For, otherwise the formation of the corresponding disulphonium compounds is inexplicable.

It has been shown in the previous communication that $[3(SHgNO_2)HgO]_2$ alone, by interacting with alkyl iodides, gives disulphonium compounds of the type $[R_2S_2, HgI_2, RI]$ (T. 1917, ***111***, 108).

So, the presence of the group (—$SHgNO_2$) is essential to the formation of disulphonium compounds, whether it be present as such as in $[3(SHgNO_2)HgO]_2$ or associated with simple alkyl groups as in $EtSHgNO_2$ or in complex groups as in



EXPERIMENTAL

Interaction of N-Phenyl-Dithiobiazoline Sulphydrate and Mercuric Nitrite.

As it was difficult to obtain the mercaptan itself in a state of purity the K-salt was (Ber 27. 2516) treated with mercuric nitrite. It had the additional advantage inasmuch as no nitrous acid was liberated, which would have an oxidising action on the one or more atoms of sulphur. The mercury salt was obtained sometimes anhydrous, but often combined with three, five and eight molecules of water; the degree of hydration, evidently depending upon the dilution of the reacting substances, the anhydrous variety had a deep yellow colour while the compound containing the largest number of water molecules (*viz.* eight) was almost white. They all evolved nitrous fumes when treated with hydrochloric acid. It may be added here once for all, that these as also the following compounds were always dried in a vacuum over sulphuric acid.

Results of analysis:—

0·2724 gave 0·1187 Hg; Hg=43·59.

0·1100 gave 0·0810 CO_2 and 0·0187 H_2O; C=20·08; H=1·89.

0·1420 gave 10·2 c.c. N_2 at 25°c and 760 mm; N=8·10.

Calc. for $C_8H_5N_3S_3HgO_2$: Hg=42·46; C=20·38; H=1·06; N=8·92.

*The above with 3 H_2O:—

found Hg=38·05; C=18·28; H=3·29; N=8·30; S=18·56.

Calc. Hg=38·09; C=18·29; H=2·1; N=8·00; S=18·29.

The compound with 5H_2O:—

found Hg=35·75; C=16·92; H=3·20.

Calc. Hg=35·65; C=17·12; H=2·67.

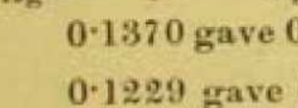
The compound with 8H_2O:—

found Hg=32·10; C=15·10; H=3·56; N=6·16; S=15·08.

Calc. Hg=32·52; C=15·63; H=3·41; N=6·83; S=15·61.

Mercuric nitrite and thiobiazole-disulphydrate :

As a rule the product which is the outcome of the condensation of three molecules of thiobiazole-disulphydrate is formed. It is only in rare cases that the condensation with four molecules takes place. As in the case of the previous compounds different number of water molecules are associated with the molecule, the degree of hydration depending upon the concentration of the reacting substances. The product formed by condensation of three molecules, *viz.*,



$$\begin{array}{ccc} S-(C_2N_2S)_3S_4 & - & S \\ | & & | \\ Hg & —O— & Hg \end{array}$$

, 8H_2O gave the following results on analysis:—

0·1370 gave 0·0639 HgS and 0·2749 $BaSO_4$; Hg=40·21, S=27·56.

0·1229 gave 0·0383 CO_2; C=8·50.

0·1377 gave 10·2 c.c.N_2 at 30°c and 760 mm; N=8·18.

Calc. Hg=39·85; S=28·69; C=7·17; N=8·37.

---

* In order to economise space details of the results of analysis of the hydrated varieties are not given. It is necessary to point out here also that the percentage of hydrogen in most cases comes out unusually high as traces of mercurial vapour are apt to be carried into the $CaCl_2$ tube.

The above with $5H_2O$:—

0·2010 gave 0·0981 HgS and 0·4421 $BaSO_4$; Hg=42·07; S=30·21.

0·1592 gave 13·36 c.c. N_2 at 32°c and 760 mm.; N=9 36

Calc. Hg=42·11; S=30·31; N=8·84.

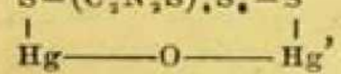
The above with $2H_2O$:—

0·1392 gave 0·0732 HgS and 0·3182 $BaS0_4$; Hg=45·33; S=31·40.

0·1865 gave 16 c. c. of N_2 at 29°c and 760 mm ; N=9·52.

Calc. Hg=44·65; S=32·14; N=9·38.

The compound formed by condensation of four molecules, *viz.*,



$\begin{array}{l} S-(C_2N_2S)_4S_4-S \\ \mid \qquad\qquad\qquad \mid \\ Hg \text{———} O \text{———} Hg \end{array}$, $+3H_2O$ gave the following results of analysis:—

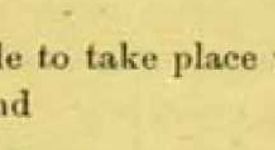
0·2800 gave 0·1064 Hg and 0·7654 $BaSO_4$; Hg=37·94; S=37·54

0·0904 gave 9·4 c.c. N_2 at 30°C and 760 mm ; N=11·48

Calc. Hg=37·67 ; S=36·16 ; N=10·55

Interaction of mercuric nitrite with the potassium salt of thiobiazoledisulphydrate :

When the reaction is made to take place with the freshly dissolved K-salt in water, the compound



is formed. The product is a greenish yellow nitrite and gave the following results on analysis:—

0·3037 gave 0·1714 HgS and 0·5702 $BaSO_4$; Hg=48·65 S=25·79

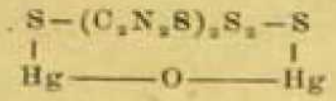
0·1658 gave 12·6 c.c. N_2 at 31° and 760 mm ; N=8·37

Calc. Hg=46·19 ; S=22·17 ; N=9·70

The presence of potassium was also proved. The salt thus approaches almost the theoretical formula given above ; but it is necessarily contaminated with a slight admixture of the next compound.

On keeping, the potassium salt undergoes hydrolysis in aqueous solution as is proved by its alkalinity. In two preparations greenish-yellow precipitates were obtained.

The compound conforms to the formula



$$\begin{array}{ccc} S-(C_2N_2S)_2S_2 & - & S \\ | & & | \\ Hg & -O- & Hg \end{array}$$

with a slight admixture of prep. I.

0·1626 gave 0·0986 HgS and 0·2624 $BaSO_4$; Hg=52·28; S=22·35

0·1620 gave 10·8 c.c. N_2 at 32°c and 760 mm; N=7·36

Calc. for the pure compound, Hg=56·12; S=26·97; N=7·86

Mercuric nitrite and thiophenol :

Three different compounds have been isolated in this case. When the alcoholic solution of thiophenol is added very slowly to an excess of mercuric nitrite solution the reaction takes the ordinary course and $PhSHgNO_2$ is mainly formed. It is a dull yellow, light granular powder and is a real nitrite. But, when the thio-compound is in excess and the addition does not take place very slowly, the whole of the reaction mixture assumes a dirty yellow colour and nitrous fumes are evolved profusely. On standing, however, the reaction subsides and a white granular powder is obtained. It can be crystallised from hot benzene and when absolutely pure has a sharp m. p. 140°. Under slightly varying conditions an oxy-compound $[(PhS)_3HgO]_2]$ is formed. As is evident, it is not easy to control the reaction so as to give one product to the complete exclusion of the others. The nitrite-mercaptide is always found to be admixed with the other products of this reaction.

The nitrite-mercaptide gave different results of analysis on different occasions, depending upon the proportion of Ph_2S_3Hg admixed with it; generally, however, the values have been found to be intermediate between that of the pure compound and Ph_2S_3Hg.

	Calc. for $PhSHgNO_2$	found	Calc. for Ph_2S_3Hg.
Hg =	56·33	51·30	44·44
S =	9·01	14·23	21·30
C =	20·28	26·44	32·00
H =	1·41	2·24	2·30

It will be noticed that the substance consisted of almost equal proportions of both.

The compound of the formula Ph_2S_3Hg gave the following results on analysis :—

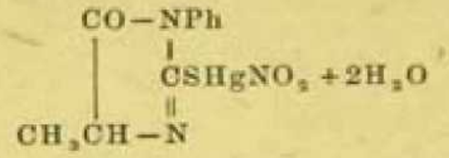
0·1942 gave 0·0864 Hg and 0·3134 $BaSO_4$; Hg = 44·48 ; S = 22·16.
0·0964 gave 0·116 CO_2 and 0·0230 H_2O; C = 32·17 ; H = 2·7.
Calc. Hg = 44·44 ; S = 21·30 ; C = 32·00 ; H = 2·30.

The compound $[3(PhS)HgO]_2$ gave the following results on analysis :—

0·4016 gave 0·1506 Hg ; Hg = 37·50
0·4333 gave 0·5620 $BaSO_4$; S = 17·82
0·1230 gave 0·1886 CO_2 ; C = 41·81
Calc. Hg = 38·02 S = 18·25 ; C = 41·07

The above two compounds were proved to be non-nitrogenous by combustion analysis.

Mercuric nitrite and phenyl-methyl-thiohydantoin : formation of the compound :

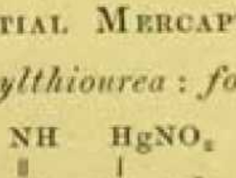


The compound was greenish-grey in colour and was a real nitrite.

0·1981 gave 0·0954 HgS and 0·1110 $BaSO_4$; Hg = 41·51 ; S = 7·69
0·1774 gave 0·1586 CO_2 and 0·0582 H_2O ; C = 24·38 ; H = 3·65.
0·2836 gave 20·8 c. c. N_2 at 30° and 760 mm ; N = 8·10
Calc. Hg = 41·07 ; S = 6·57 ; C = 24·64 ; H = 1·85 ; N = 8·63.

POTENTIAL MERCAPTANS.

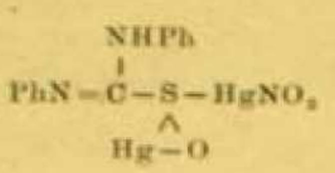
Mercuric nitrite and phenylthiourea : formation of the compound :



In this case the tendency to form into a pasty mass is well marked and it was with great difficulty and after several failures that the pure product was obtained. It was deep yellow in colour and was a nitrite.

0·3512 gave 0·2350 Hg and 0·1227 $BaSO_4$; Hg = 66·9 ; S = 4·8
0·2015 gave 11·4 c. c. N_2 at 26° and 760 mm ; N = 6·40
Calc. Hg = 65·25 ; S = 5·22 ; N = 6·85.

Mercuric nitrite and sym-diphenyl thiourea; formation of the compound:



$$\begin{array}{c}\mathrm{NHPh}\\ |\\ \mathrm{PhN{=}C{-}S{-}HgNO_2}\\ \wedge\\ \mathrm{Hg{-}O}\end{array}$$

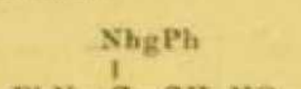
It was a brownish yellow granular powder, and was a nitrite.

0·3422 gave 0·1970 Hg and 0·1069 $BaSO_4$; Hg=57·57 ; S=4·64

0·3970 gave 0·1141 CO_2 and 0·0244 H_2O ; C=22·27 ; H=1·94

Calc. Hg=58·07 ; S=4·64; C=22·64 ; H=1·60.

The above compound is only rarely formed. The product generally obtained conforms to the formula



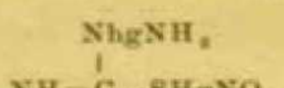
$$\begin{array}{c}\mathrm{NhgPh}\\ |\\ \mathrm{PhN{=}C{-}SHgNO_2}\end{array}$$

0·1555 gave 0·0947 HgS and 0·0741 $BaSO_4$; Hg=52·51 ; S=6·55

0·2275 gave 0·1367 HgS and 0·0992 $BaSO_4$; Hg=51·80 S=5·99

Calc. Hg=52·43; S=5·59.

Mercuric nitrite and thiosemicarbazide: formation of the compound:



$$\begin{array}{c}\mathrm{NhgNH_2}\\ |\\ \mathrm{NH{=}C{-}SHgNO_2}\end{array}$$

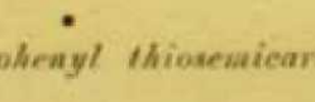
The thio-compound was taken in aqueous solution. The product was a dull yellow granular powder and was a nitrite.

0·2715 gave 0·1870 HgS and 0·1362 $BaSO_4$; Hg=68·87 ; S=6·89

0·1032 gave 11·8 c. c. N_2 at 32°c and 760 mm ; N=12·6

Calc. Hg=68·96 ; S=7·36 ; N=12·87.

Mercuric nitrite and phenyl thiosemicarbazide: formation of the compound:



$$\begin{array}{c}\mathrm{NhgNHPh}\\ |\\ \mathrm{NH{=}C{-}SHgNO_2}\end{array}$$

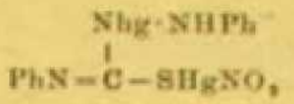
It is an orange yellow granular powder and is a nitrite.

0·3081 gave 0·1824 Hg and 0·1326 $BaSO_4$; Hg=59·2 ; S=5·91

0·2036 gave 20·5 c. c. N_2 at 33° and 760 mm ; N=11·10

Calc. Hg=58·70 ; S=6·26 ; N=10·96.

Mercuric nitrite and diphenyl thiosemicarbazide: formation of the compound :



$$\begin{array}{l}\qquad\quad\text{Nhg}\cdot\text{NHPh}\\ \qquad\quad|\\ \text{PhN}=\text{C}-\text{SHgNO}_2\end{array}$$

It is an orange yellow granular powder and is a nitrite.

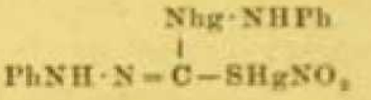
0·1797 gave 0·0923 Hg ; Hg=51·48.

0·2577 gave 0·2498 CO_2 and 0·0523 H_2O ; C=26·21 ; H=2·25.

0·1380 gave 11·7 c. c. N_2 at 32° and 760 mm ; N=9·38.

Calc. Hg=51·11 ; C=28·57 ; H=1·87 ; N=9·54.

Mercuric nitrite and diphenyl sulpho-carbazide: formation of the compound :



$$\begin{array}{l}\qquad\qquad\quad\text{Nhg}\cdot\text{NHPh}\\ \qquad\qquad\quad|\\ \text{PhNH}\cdot\text{N}=\text{C}-\text{SHgNO}_2\end{array}$$

It is a beautiful pink coloured granular powder and is a nitrite.

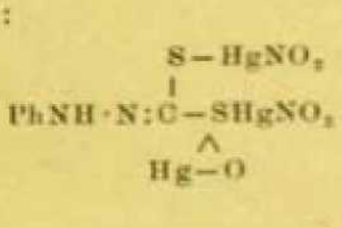
0·1667 gave 0·0965 HgS and 0·0607 $BaSO_4$; Hg=49·91; S=5·00

0·1463 gave 0·1404 CO_2 and 0·0327 H_2O; C=26·14; H=2·48.

0·1167 gave 11·7 c. c. N_2 at 30° and 760 mm ; N=11·26.

Calc. Hg=49·83 ; S=5·31 ; C=25·91 ; H=1·82 ; N=11·62.

Mercuric nitrite and phenyl dithiocarbazinic acid phenylhydrazine: formation of the compound :



$$\begin{array}{l}\qquad\qquad\quad\text{S}-\text{HgNO}_2\\ \qquad\qquad\quad|\\ \text{PhNH}\cdot\text{N}:\text{C}-\text{SHgNO}_2\\ \qquad\qquad\quad\;\wedge\\ \qquad\qquad\text{Hg}-\text{O}\end{array}$$

It is a blackish violet granular powder and is a nitrite.

0·1971 gave 0·1549 Hg and 0·1031 $BaSO_4$; Hg=67·71 ; S=7·18

0·1651 gave 8·5 c. c. N_2 at 27° and 760 mm ; N=5·89.

Calc. Hg=67·40 ; S=7·19 ; N=6·30 ; C=9·44.

Mercuric nitrite and K-phenyldithiocarbazinate: formation of the same compound as above :

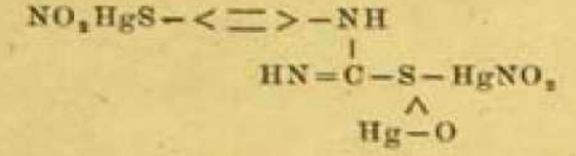
0·3294 gave 0·2239 Hg ; Hg=67·97.

0·1790 gave 0·0607 CO_2 and 0·0158 H_2O ; C=9·24 ; H=0·98

0·1321 gave 6·8 c. c. N_2 at 27° and 760 mm. N=5·88.

Calc. see above.

Mercuric nitrite and p. chloro-phenyl-thiourea : formation of the compound :



Great caution is necessary in the preparation of this compound. An acetone solution of the thio-compound is added in a thin stream under vigorous shaking to a solution of mercuric nitrite, care being taken that the latter is always in *large excess ;* otherwise, the product turns blackish, being slowly converted into mercuric sulphide. The compound was yellow and sometimes orange red and responded to the tests of a nitrite.

0·3578 gave 0·2410 Hg ; Hg.=67·37.

0·1823 gave 0·0961 $BaSO_4$; S=7·24.

0·1302 gave 0·0442 CO_2 and 0·0192 H_2O ; C=9·26 ; H=1·64.

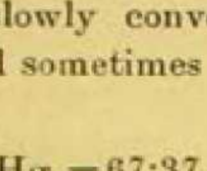
0·1448 gave 7·4 c. c. N_2 at 20° and 760 mm ; N=5·87.

Calc. Hg=67·42 ; S=7·19 ; C=9·44 ; H=0·67 ; N=6·29.

Absence of chlorine was also proved.

MIGRATION OF ALKYL RADICALS.

Mercuric nitrite and imido-phenyl-carbamic-thio-methylester : formation of the compound :



$$\begin{array}{l} NCH_3 \\ \| \\ C-SHgNO_2 \\ | \\ NHPh \end{array}$$

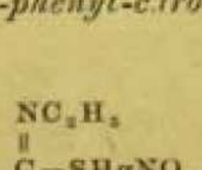
It is formed as a yellowish white flocculent precipitate which when dry turns orange yellow.

0·3050 gave 0·1464 Hg and 0·1533 $BaSO_4$; Hg=48·01 ; S=6·91

0·1461 gave 0·1238 CO_2 and 0·0329 H_2O ; C=23·10 ; H=2·51

Calc. Hg=48·42 ; S=7·75 ; C=23·24 ; H=2·18.

Mercuric nitrite and imido-phenyl-carbamic-thioethylester : formation of the compound :



$$\begin{array}{l} NC_2H_5 \\ \| \\ C-SHgNO_2 \\ | \\ NHPh \end{array}$$

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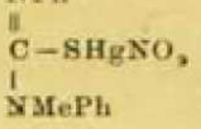
0·2918 gave 0·1340 Hg ; Hg = 45.93 ;

0·1936 gave 17·10 c. c. N_2 at 28° and 760 mm ; N = 9·92.

Calc. Hg = 46·84 ; N = 9·97.

Mercuric nitrite and phenyl imidophenyl carbamicthiomethylester: formation of the compound :



$$\begin{array}{l}\mathrm{NPh}\\ \| \\ \mathrm{C-SHgNO_2}\\ | \\ \mathrm{NMePh}\end{array}$$

It is an orange yellow granular powder and is a nitrite.

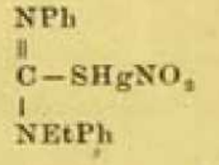
0·2801 gave 0·1038 Hg ; Hg = 39·86.

0·23·77 gave 0·3027 CO_2 and 0·0738 H_2O; C = 34·70 ; H = 3·45.

0·2863 gave 22·6 c. c. N_2 at 29°c and 760 mm. ; N = 8·99.

Calc. Hg = 40·9 ; C = 34·50 ; H = 2·67 ; N = 8·86.

Mercuric nitrite and phenylimidophenyl carbamicthioethylester: formation of the compound :



$$\begin{array}{l}\mathrm{NPh}\\ \| \\ \mathrm{C-SHgNO_2}\\ | \\ \mathrm{NEtPh}\end{array}$$

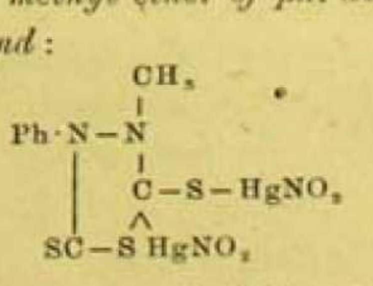
It is an orange yellow granular powder and is a nitrite.

0·3730 gave 0·1478 Hg and 0·1874 $BaSO_4$; Hg = 39 63 ; S = 6·91.

0·1232 gave 9·4 c. c. N_2 at 32° and 760 mm. N = 8·43.

Calc. Hg = 39·92 ; S = 6·39 ; N = 8·38.

Mercuric nitrite and methyl ether of ph. dithiobiazoline sulphydrate: formation of the compound :



The thio-compound was dissolved in chloroform and the clear solution thus obtained was vigorously agitated with mercuric nitrite solution for nearly half an hour, when an emulsion was formed. It was allowed to stand over-night. A cream coloured granular mass was obtained, which was thrown on filter and washed with water, alcohol

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and finally with chloroform and dried in a vacuum desiccator. It evolved nitrous fumes with HCl.

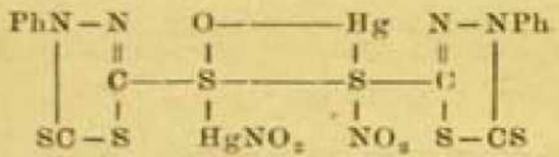
0·1984 gave 0·1055 HgS and 0·1384 $BaSO_4$; Hg = 45·85; S = 9·58.

0·1879 gave 0·0884 CO_2 and 0·0296 H_2O; C = 12·83; H = 1·75.

0·1603 gave 10·2 c. c. N_2 at 30° and 760 mm; N = 7·03.

Calc. Hg = 45·67; S = 10·96; C = 12·33; H = 0·91; N = 6·39.

Mercuric nitrite and phenyldithiobiazoline disulphide: formation of the compound:



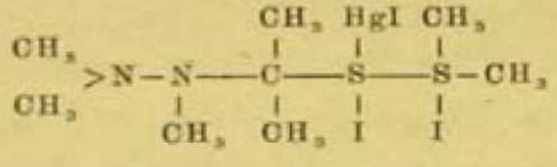
0·2940 gave 0·1288 Hg; Hg = 43·80.

0·1190 gave 9·00 c. c. N_2 at 30° and 760 mm; N = 8·35.

Calc. Hg = 41·75; N = 8·77.

INTERACTION WITH THE ALKYL IODIDES.

Mercaptide nitrite of n-phenyl-dithiobiazoline sulphydrate and methyl iodide: formation of the compound:



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>N-\underset{CH_3}{\underset{|}{N}}-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\overset{HgI}{\overset{|}{\underset{I}{\underset{|}{S}}}}-\overset{CH_3}{\overset{|}{\underset{I}{\underset{|}{S}}}}-CH_3$$

The method of procedure is exactly the same as in the interaction of mercury-mercaptide nitrites and the simple alkyl iodides. After refluxing with methyl-iodide it was found that a portion was left undissolved, which, when purified by washing several times with acetone, melted sharply at 127°C. The soluble portion (in acetone) however, had to be purified by precipitation by addition of ether, and the pure compound thus obtained melted sharply at 107°. It gave the following results on analysis:—

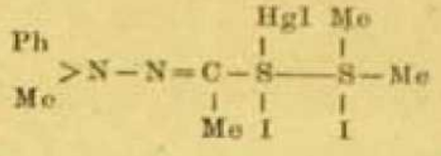
0·3129 gave 0·0811 Hg; Hg = 25·92.

0·4107 gave 0·1066 Hg and 0·3718 AgI; Hg = 25·96; I = 48·72.

0·0844 gave 0·0363 CO_2 and 0·0237 H_2O; C = 11·73; H = 2·45.

$C_8H_{21}N_2S_2HgI_3$ requires, Hg = 25·32; I = 48·23; C = 12·15; H = 2·66.

The insoluble compound (in acetone) of the formula



$$\begin{matrix}Ph\\Me\end{matrix}\!>N-N=\underset{Me}{C}-\underset{I}{\overset{HgI}{S}}-\underset{I}{\overset{Me}{S}}-Me$$

m.p. 127°, gave the following results on analysis :—

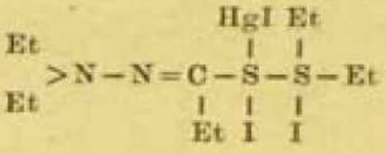
0·1867 gave 0·0449 Hg, 0·1527 AgI and 0·0870 $BaSO_4$; Hg = 25·96 ; I = 48·93 ; S = 6·40.

0·1070 gave 0·0590 CO_2 and 0·0734 H_2O ; C = 15·06 ; H = 1·39.

0·1227 gave 4·2 c. c. N_2 at 30° and 760 mm. ; N = 3·73.

$C_{11}H_{17}N_2S_2HgI_3$, requires, Hg = 24·33 ; I = 46·35 ; S = 7·79 C = 16·06 ; H = 2·87.

The above mercaptide nitrite and ethyl iodide; formation of the compound:



$$\begin{matrix}Et\\Et\end{matrix}\!>N-N=\underset{Et}{C}-\underset{I}{\overset{HgI}{S}}-\underset{I}{\overset{Et}{S}}-Et$$

In this case also, the soluble portion (in acetone) was purified by repeated crystallisation. The pure compound was a dull yellow crystalline powder and melted sharply at 73-74°c.

0·2316 gave 0·0572 Hg, 0·1960 AgI and 0·0972 $BaSO_4$; Hg = 24·69 ; I = 45·74 ; S = 5·77.*

0·2564 gave 0·0611 Hg ; Hg = 23·83.

0·1278 gave 0·0703 CO_2 and 0·0296 H_2O ; C = 15·41 ; H = 2·58.

0·2470 gave 7·8 C.C. N_2 at 31° and 760 mm ; N = 3·50.

$C_{11}H_{25}N_2S_2HgI_3$ requires, Hg = 24·09 ; I = 45·9 ; S = 7·71 C = 15·9 ; H = 3·07 ; N = 3·57.

The above three preparations were repeated at least half a dozen times, and in each case, sharply defined compounds of the above composition were obtained.

Phenyl mercaptide nitrite and methyliodide: formation of the compound, $[PhMeS_2, HgI_2, MeI.]$

The pure product was obtained by repeated crystallisation and was a dull yellow crystalline powder, m.p. 90°.

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* *Vide*, foot-note, p. 26.

0·4616 gave 0·1252 Hg and 0·4353 AgI ; Hg = 27·12 ; I=50·96.

0·1131 gave 0·0551 CO_2 ; C = 13·29.

$C_8H_{11}S_2HgI_3$ requires, Hg = 26·6 ; I = 50·66 ; C = 12·77.

Phenyl mercaptide nitrite and ethyl iodide : formation of the compound [$PhEtS_2$, HgI_2, EtI.]

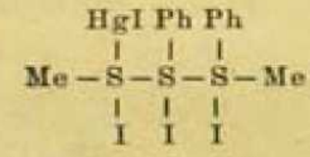
The soluble portion (in acetone) in this case, first of all appeared as a greenish yellow oil, which soon crystallised on stirring and had the m.p. 59°.

0·2994 gavo 0·0774 Hg and 0·2673 Ag I ; Hg=25·85 ; I=48·24.

0·1302 gave 0·0740 CO_2 and 0·0282 H_2O ; C = 15·5 ; H=1·86.

$C_{10}H_{15}S_2HgI_3$ requires, Hg = 25·64 ; I=48·84 ; C=15·39; H = 1·92.

Ph_2S_3Hg and methyl iodide : formation of the compound :



$$\mathrm{Me-\underset{I}{\overset{HgI}{S}}-\underset{I}{\overset{Ph}{S}}-\underset{I}{\overset{Ph}{S}}-Me}$$

The product was an oil, which on stirring crystallised *en masse.* It was washed several times with acetone when the colour turned to yellowish white. It was insoluble in acetone and melted sharply at 111-112°.

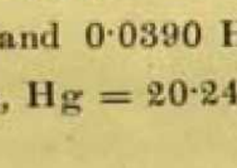
0·3150 gave 0·0615 Hg, 0·2915 AgI and 0·2007 $BaSO_4$; Hg=19·53 ; I = 50·00 ; S = 8·75.

0·1410 gave 0·0902 CO_2 and 0·0390 H_2O. C=17·41 ; H=3·07

$C_{14}H_{16}S_3HgI_4$ requires, Hg = 20·24 ; I = 51·42 ; S = 9·71 ; C = 17·00 ; H = 1·62.

It will be noticed that whenever a sulphonium compound contains phenyl groups, it becomes insoluble in acetone.

Mercaptide nitrite of thiocarbanilide and ethyl iodid : formation of the compound :



$$\mathrm{I-\underset{Et}{\overset{Et}{C}}-\underset{I}{\overset{Et}{S}}-HgI}$$

In this case a deep purple-coloured needle-shaped crystalline product was obtained. It was soluble in acetone.

0·3083 gave 0·0890 Hg, 0·2920 AgI and 0·1042 $BaSO_4$; Hg=28·73; I=51.18; S=4.64.

0·1214 gave 0·0552 CO_2 and 0·0232 H_2O; C=12·04; H=2·12.

$C_7H_{15}SHgI_3$ requires; Hg=28·09; I=53·51; S=4·49; C=11·8; H=2·11.

Mercaptide nitrite of phenyl imido-phenylcarbamicthiomethylester and Methyl iodide: formation of the compound [Me_2S_2, HgI_2, MeI.]

The mercaptide-nitrite was refluxed with methyl iodide. Next day a yellow crystalline mass was found at the bottom of the liquid. The mother liquor was drained off and evaporated on the water bath when a treacle-like mass remained. The yellow crystalline product was exhausted several times with acetone and an insoluble pale yellow crystalline residue melting at 176—180° remained. The treacle-like mass on stirring with a little acetone crystallised *en masse*. The acetone filtrate from both was concentrated to a small bulk and treated with ether when a mealy, pale yellow crystalline mass was precipitated. But, as this had no sharp melting point, it was subjected to fractional crystallisation. The fractions had melting points varying between (147—155°), (153—164°) and (160—176°). The first two were once more dissolved in acetone, filtered off the insoluble portion and again precipitated by ether. The process was repeated five or six times when at last a fairly good crop was obtained, which melted sharply at 160—162°C.

0·3290 gave 0·0791 Hg and 0·3281 AgI; Hg=29·51; I=53·89.

0·1150 gave 0·0221 CO_2 and 0·0218 H_2O; C=5·24; H=2·11.

$C_3H_9HgI_3S_2$ requires Hg=28·98; I=55·21; C=5·22; H=1·30.

From its appearance, melting point and analysis, it is thus found to be [Me_2S_2, HgI_2, MeI].

Mercaptide nitrite of phenylimidophenylcarbamicthioethyl ester and ethyl iodide: formation of [Et_2S_2, HgI_2, EtI.]

The procedure was almost the same as in the previous instance. On concentrating the acetone solution a portion crystallised out, which had no sharp m.p. (*viz.*, 100-138°).

It was purified by repeated fractional crystallisation; when absolutely pure, it melted sharply at 110-111°.

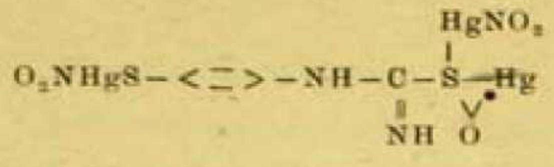
0·3127 gave 0·0862 Hg and 0·0978 AgI; Hg=27·57; I=51·46

0·2740 gave 0·0758 Hg; Hg=27·66

0·0861 gave 0·0327 CO_2 and 0·0255 H_2O; $C=10{\cdot}37$; $H=3{\cdot}29$

$C_6H_{15}S_2HgI_3$ requires, $Hg=27{\cdot}32$; $I=52{\cdot}05$; $C=10{\cdot}37$; $H=3{\cdot}29$

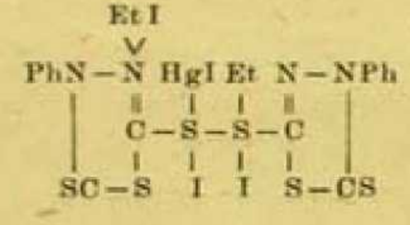
Mercaptide nitrite from the p. chlorophenylthiourea derivative, viz.,



and ethyl iodide: formation of the compounds:

$(SHgI)_2$ and $[Et_2S_2, HgI_2, EtI]$ which agreed with the analysis already published (l.c.p. 109). The di-mercuri-di-iodo-disulphide had reversible phototropic properties.

Phenyl dithiobiazoline disulphide, mercuric iodide and ethyl iodide: synthesis of the compound:



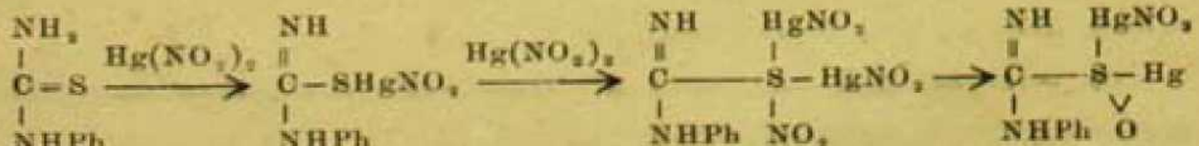
0·3127 gave 0·0512 Hg, 0·2366 AgI and 0·3026 $BaSO_4$; $Hg=16{\cdot}38$; $I=40{\cdot}89$ and $S=13{\cdot}29$*

0·1574 gave 0·1066 CO_2; $C=18{\cdot}47$.

Calc. $Hg=16{\cdot}45$; $I=41{\cdot}75$; $S=15{\cdot}79$; $C=19{\cdot}74$.

SUMMARY AND CONCLUSION—ENUNCIATION OF LAWS.

From the present investigation it is found (1) that mercuric nitrite acting upon the aryl substituted thiocarbamides brings about their tautomerisation and the divalent sulphur atom thereby acquires additional energy and the capacity to take up the radicals of $Hg(NO_2)_2$, becoming tetravalent, thus :—



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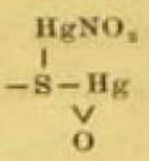
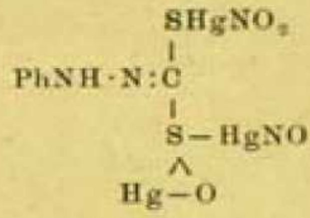
* Owing to the tedious process involved, the sulphur and iodine sometimes came out too low (*vide* "Trans. Chem. Soc." 1916, *109*, p. 135).

(2) That one and the same atom of sulphur cannot retain the load of one $Hg(NO_2)_2$ and an additional ($-HgNO_2$) groups, but by parting with N_2O_3 becomes an oxynitrite



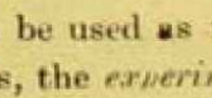
$$\begin{array}{c} HgNO_2 \\ | \\ -S-Hg \\ \vee \\ O \end{array}$$

(3) that sometimes, however, mercuric nitrite acts in a twofold character. Not only does it bring about tautomeric changes as indicated above but an atom of hydrogen in the imino-group is simultaneously replaced by its equivalent of (hg); in such cases, the molecule being already loaded with ($-HgNO_2$) and (hg), the sulphur atom can no longer become tetravalent by taking up a fresh load of $Hg(NO_2)_2$ (Cf. derivatives of diphenyl-thiocarbamide, thiosemicarbazide, etc., p. 6). If, however, there be two mercaptanic sulphur atoms in the molecule, one real and the other potential, then each of these sulphur atoms can individually take up its own quota of $HgNO_2$; *e.g.*,



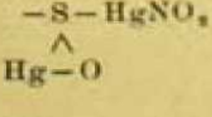
$$\begin{array}{l} \qquad\qquad\quad SHgNO_2 \\ \qquad\qquad\quad | \\ PhNH \cdot N{:}C \\ \qquad\qquad\quad | \\ \qquad\qquad\quad S-HgNO_2 \\ \qquad\qquad\quad \wedge \\ \qquad\qquad Hg-O \end{array}$$

(4) that a mercaptan, however complex its structure might be—provided it is a real mercaptan—does not undergo disruption but has simply the H of SH replaced by ($-HgNO_2$). If, however, the compound be a potential mercaptan, even if its molecule be of a simple character, *e.g.*, thiocarbamide, it either undergoes disruption or its sulphur atom in view of the superadded energy becomes tetravalent, *i.e.*, $-SHgNO_2$ becomes



$$\begin{array}{l} -S-HgNO_2 \\ \quad \wedge \\ Hg-O \end{array}$$

(5) that mercuric nitrite can be used as reagent for the diagnosis of real and potential mercaptans, the *experimentum crucis* being furnished by salts of phenyl sulphocarbazinic acid, which is at once a real and a potential mercaptan and as such the hydrogen attached to the mercaptanic S is simply replaced by ($-HgNO_2$), whereas, the S of the potential mercaptan possessing additional energy passes on to the tetravalent form, *viz.*,



$$\begin{array}{l} -S-HgNO_2 \\ \quad \wedge \\ Hg-O \end{array}$$

(6) that so great is the affinity of S for the group $(-HgNO_3)$, that it pushes the alkyl radical attached to it to the adjacent nitrogen atom and thus also brings about migration of alkyl radicals.

(7) that the sulphur atoms forming the ring does not possess the property of becoming tetravalent by adding on the radicals of $Hg(NO_3)_2$.

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INTERACTION OF MERCURIC, PLATINIC AND CUPRIC CHLORIDE RESPECTIVELY WITH THE MERCAPTANS AND POTENTIAL MERCAPTANS.

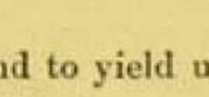
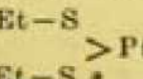
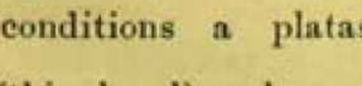
BY

PRAFULLA CHANDRA RÂY.

INTRODUCTORY

SOME four years ago, the author ventured to put forth the view that the compounds which mercuric, platinic and cupric chloride respectively yield with thiocarbamide and thioacetamide, etc., are of the same nature as those obtained by the interaction of these halides with real mercaptans; *i.e.*, they are chloromercaptides (Proc. Chem. Soc., 1914, *30*, 304). Since then extended investigations have been carried on in this field especially through the aid of mercuric nitrite, (T., 1917, *111*, 101), a reagent which brings about ready tautomeric changes. Iodine also has been found to act similarly on these bodies (Trans. Chem. Soc., 1916, *109*, 698), inasmuch as they behave like iminomercaptans.

It seemed desirable at the outset to undertake a systematic study of the behaviour of mercuric, cupric and platinic chlorides towards some of the typical mono-, and di-mercaptans, namely, ethyl and ethylene mercaptans, phenyldithiobiazoline sulphydrate and thiobiazol disulphydrate.

Ethyl mercaptan has been found to yield under normal conditions a chloromercaptide of the formula  $\begin{matrix}\mathrm{Et{-}S}\\ \mathrm{Et{-}S}\end{matrix}\!>\!\mathrm{Pt{-}Cl}$ and under exceptional conditions a plataso-mercaptide  $\begin{matrix}\mathrm{Et{-}S}\\ \mathrm{Et{-}S}\end{matrix}\!>\!\mathrm{Pt}$. Ethylene mercaptan (thioglycol) also yields a chloro-mercaptide of the formula  $C_2H_4\!<\!\begin{matrix}S\\ S\end{matrix}\!>\!Pt\!<\!\begin{matrix} & S-C_2H_4\\ & \mid\\ Cl & SH\end{matrix}$. In the formation of this remarkable compound, two molecules of thioglycol simultaneously take part in the reaction; one atom of chlorine of the platinic chloride remains, however, intact.

Phenyldithiobiazoline sulphydrate or rather its potassium salt has been found to be equally reactive towards platinic chloride and it readily yields mercaptides in which platinum functions both as a triad and a diad element as in the case of the simple ethyl mercaptan.

The valency of platinum calls for a few remarks. The salts of the type MX_3 are scarcely represented among the platinum compounds. In the formula $\begin{matrix}Et-S\\Et-S\end{matrix}>Pt-Cl$, platinum, no doubt, may be made to appear as tetravalent by doubling it. Platinum has its proper place in the eighth or transitional group in the periodic system, which also includes iron and iridium. Now, the chlorides of these metals are represented by the simple formula MCl_3 and not by M_2Cl_6. Moreover, platinum with high atomic weight of 194 will have scarcely two atoms coalesced into the complex $\equiv Pt—Pt \equiv$. Salts containing two atoms of platinum in the molecule have, it is true, been described, but they are of a very complex character.*

The product of the reaction of mercuric chloride with thiocarbamide has been assigned the formula $HgCl_2CSN_2H_4$ (Rosenheim and Meyer, *Zeit., Anorg. Chem.*, 1903, *34*, 62; Ibid, 1906, *49*, 13). In other words, it has been regarded as a mere additive or molecular compound. From considerations based upon analogy the author suggested that it should be formulated as $\left(\begin{matrix}NH_2-\underset{\underset{NH}{\parallel}}{C}-S-HgCl\end{matrix}\right)HCl$; *i.e.*, it is the product of the reaction of mercuric chloride upon ψ thiocarbamide (imino-mercaptan). The hydrogen chloride, which is formed, is not liberated in the free state but is simply fixed by the basic complex. It is well-known that formamidine disulphide exists as a salt of a diacid base because of the presence of the amino- and imino- radicals. Convincing proof has recently been obtained in support of the above formula. The compound in question has been found to be sufficiently soluble in water to admit of conductivity measurements. If it were an additive one, in solution it would simply break up into its components. Now, thiocarbamide is practically a non-electrolyte and mercuric chloride is very feebly ionised in solution (Cf. Rây & Dhar, T., 1913, *103*, 8). The aqueous solution, however, shows an enormous increase in the dissociation, which is of the same order as that of ammonium chloride, proving that the salt is the hydrochloride of a base.

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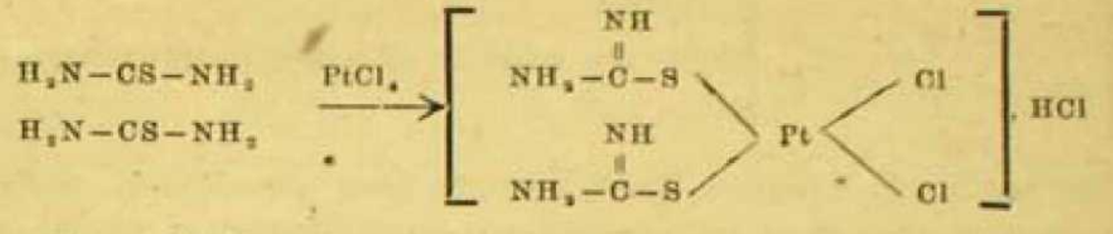
* Cosso, Ber. *23* (1890), 2503, Cleve, Bull Soc. Chem. *17* (1872), 289.

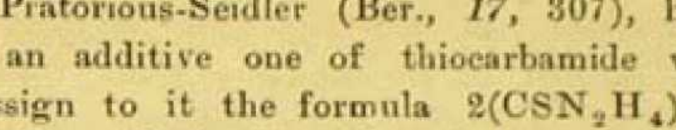
Thiocarbamide may be expected to behave in like manner towards platinic chloride and yield a compound of the same type; thus :—



$$\begin{matrix} H_2N-CS-NH_2 \\ H_2N-CS-NH_2 \end{matrix} \xrightarrow{PtCl_4} \left[\begin{matrix} NH_2-\overset{NH}{\overset{\|}{C}}-S \\ NH_2-\overset{NH}{\overset{\|}{C}}-S \end{matrix} > Pt < \begin{matrix} Cl \\ Cl \end{matrix} \right] .HCl$$

Reynolds and Prätorious-Seidler (Ber., *17*, 307), however, make the compound an additive one of thiocarbamide with platinous chloride and assign to it the formula $2(CSN_2H_4)PtCl_2,HCl$ or $2(CSN_2H_4)PtHCl_3$. That this view of the constitution of the compound is erroneous is evident from another consideration. The platinic chloride on being reduced to the platinous state would set free chlorine, which would, in turn, act upon a portion of the thiocarbamide and foramidine di-sulphide hydrochloride would be simultaneously formed;* the derivative in question is, however, free from it.

Cupric chloride is analogous in its behaviour towards thiocarbamide :—



$$CS<\begin{matrix} NH_2 \\ NH_2 \end{matrix} \xrightarrow{CuCl_2} NH_2-\underset{NH}{\underset{\|}{C}}-S-CuCl$$

In this case, however, the hydrogen chloride is liberated in the free state and has actually been detected in the filtrate. This is what might have been expected. The chlorides of mercury, platinum and cobalt have the capacity to form complex compounds with ammonia, amines and amino-groups, which, on account of their basic character, can fix a molecule of hydrogen chloride; while copper being a more positive metal does not possess this property.†

The view taken above offers also a ready interpretation of the reaction between platinic chloride and thioacetamide, first studied by Kernakow (Journ. Rus. Chem. Soc., *25*, 613). The Russian chemist formulates the compound as $PtCl_2, 4C_2H_5NS, PtCl_4$ i.e., an additive one of four molecules of thioacetamide with one of platinous chloride and another of plantinic chloride. This formula, when halved, stands as $PtCl_3, 2C_2H_5NS$, and is in reality

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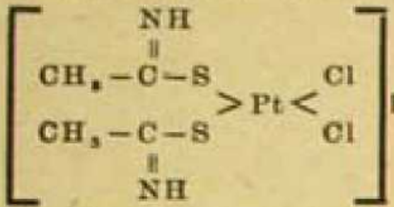
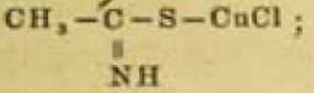
* It has been actually found that sulphuryl dichloride, which acts as a mild chlorinating agent, behaves exactly like iodine towards thiocarbamide and yields the hydrochloride of the base.

† The ammonical compounds of copper are quite distinct from those of platinum and cobalt; the latter come under Werner's supplementary valencies.



$$\left[\begin{array}{c} CH_3-\overset{\overset{NH}{\|}}{C}-S \\ CH_3-\underset{\underset{NH}{\|}}{C}-S \end{array} > Pt < \begin{array}{c} Cl \\ Cl \end{array}\right] HCl,^{*}$$

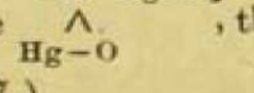
the platinic chloride functioning exactly like mercuric chloride. Thioacetamide here also simply undergoes tautomeric change. One strong argument in favour of the suggested constitution is afforded by the fact that, if platinic chloride were actually to be reduced to the platinous form, the available atoms of chlorine would act upon two other molecules of thioacetamide. It has already been shown that iodine, acting upon thioacetamide, completely breaks it up, the whole of the sulphur being precipitated. (T., 1916, *109*, 698). The product, in question, when treated with carbon bisulphide, however, did not give any sulphur. The corresponding cupric chloride derivative has been found to conform to the formula



$$CH_3-\underset{\underset{NH}{\|}}{C}-S-CuCl$$

; it is, in fact, a chloromercaptide.

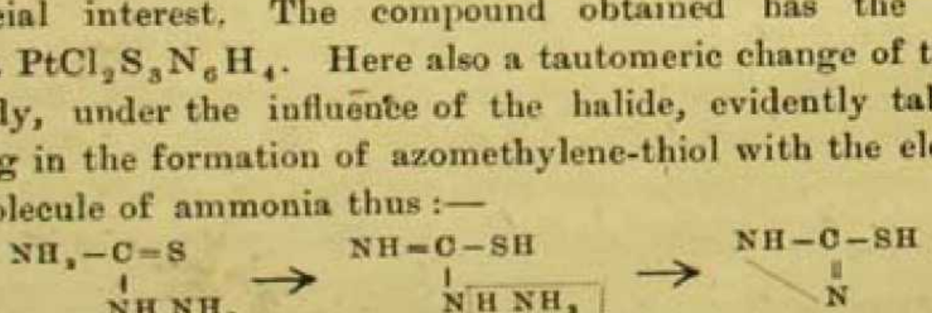
Attention may be drawn here to one striking contrast in the deportment of mercuric nitrite and chloride respectively towards these potential mercaptans ; both equally bring about tautomerisation and the initial products are $R-S-HgNO_2$ and $R-S-HgCl$ respectively ; but the former on account of its readiness to take up an additional molecule of $Hg(NO_2)_2$ undergoes a break-up and assumes the form of a sulphoxy nitrite



$$\begin{array}{c} -S-HgNO_2 \\ \wedge \\ Hg-O \end{array}$$

, the sulphur atom becoming tetravalent. (See above p. 27.)

The reaction between platinic chloride and thiosemicarbazide is of special interest. The compound obtained has the empirical formula $PtCl_2S_3N_6H_4$. Here also a tautomeric change of the parent thio-body, under the influence of the halide, evidently takes place, resulting in the formation of azomethylene-thiol with the elemination of a molecule of ammonia thus :—



$$NH_2-\underset{\underset{NH\,NH_2}{|}}{C}=S \rightarrow NH=\underset{\underset{NH\,NH_2}{|}}{C}-SH \rightarrow NH-\underset{\underset{N}{\|}}{C}-SH$$

$$\xrightarrow{PtCl_4}\left[(NH-\underset{\underset{N}{\|}}{C}-S)_2 \equiv Pt-Cl\right]HCl$$

---

* In this formula there is a deficiency of only one atom of hydrogen.

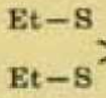
The mercaptan now acts upon platinic chloride in the usual manner, the resulting product being a chloromercaptide. Of the three molecules of hydrogen chloride generated, one is fixed by the complex body because of its basic character due to the presence of several imino-residues.

EXPERIMENTAL.

I.

MERCAPTANS AND METALLIC HALIDES.

(a) Ethyl mercaptan and platinic chloride.

Hofmann and Rabe (Zeit. Anorg. Chem., 1897, *14*, 294) maintain that if to chloroplatinic acid be added ethyl mercaptan in alcoholic solution, at first an orange yellow platinimercaptide $Pt(SEt)_4$ is formed which, when heated to 100° in a vacuum, readily yields plataso-mercaptide. It has been found, however, that by the interaction of platinic chloride and ethyl mercaptan, a platini-chloromercaptide of the formula  $\begin{matrix}Et-S\\Et-S\end{matrix}\!>Pt-Cl$ is almost invariably formed and that it is only under exceptional conditions that a platasomercaptide $Pt\,(SEt)_2$ can be obtained. If the components be added in a half-hazard manner, a mixture of the two compounds in varying proportions is formed. The *modus operandi* is therefore given here somewhat in detail. A concentrated solution of chloro-platinic acid in alcohol is taken and a very dilute solution of ethyl mercaptan in alcohol is added to it from time to time under vigorous shaking; for the first few moments, only a deep orange coloration is noticed, but shortly after a precipitate begins to put in an appearance. Care should be taken that the platinic chloride be always in sufficient excess. The orange yellow precipitate is allowed to settle for half an hour and sucked on the filter pump and washed preferably with alcohol and dried in a vacuum. If the conditions of reaction be reversed, *i.e.*, if a dilute solution of platinic chloride in small instalments be added to an excess of a concentrated solution of ethyl mercaptan, under vigorous shaking, for a few minutes the solution remains clear, after which a yellow salt begins to separate out, which is very nearly pure platasomercaptide $Pt\,(SEt)_2$.

Result of Analysis.

Prep. 1. 0·050 gave 0·0276 Pt, 0·022 AgCl and 0·065 $BaSO_4$.*
Pt=55·20 ; Cl=11·33 ; S=17·85.

Prep. 2. 0·0502 gave 0·0283 Pt and 0·0375 $BaSO_4$.
Pt=56·37 ; S=18·47.

Prep. 3. 0·0226 gave 0·0126 Pt. ∴ Pt=55·75.

Prep. 4. 0·0258 gave 0·0145 Pt. ∴ Pt=56·2.

	Found				Calc. for $(EtS)_2$ PtCl.
	1	2	3	4	
Pt	55·2	56·37	55·75	56·2	55·02
Cl	11·33	...	...	...	10·09
S	17·85	18·47	...	...	18·19

Plataso-mercaptide $Pt(SEt)_2$.

0·1317 gave 0·0814 Pt, 0·012 AgCl and 0·1985 $BaSO_4$.

	Found	Calc.
Pt	61·81	61·43
Cl	2·25	...
S	20·71	20·24

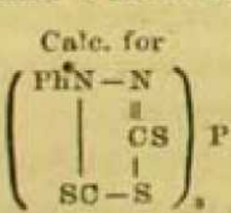
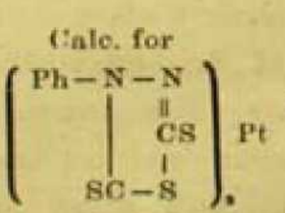
Contamination with distinct traces of the previous compound, which is invariably formed, accounts for the presence of chlorine.

(*b*) *Phenyl-dithiobiazoline sulphydrate and platinic chloride.*

The potassium salt of the mercaptan was used. To a concentrated aqueous solution of it was added under stirring a dilute solution of chloro-platinic acid in a thin stream. A yellow precipitate came down, which on drying became orange. Here also, as in the case of ethyl mercaptan, the platinum atom functions as trivalent and divalent.

Result of Analysis.

0·980 gave 0·0213 Pt and 0·1805 $BaSO_4$.

	Found	Calc. for 	Calc. for 	Mean.
Pt	26·63	22·33	30·12	26·23
S	31·00	33·14	29·18	31·16

Chlorine was found to be absent.

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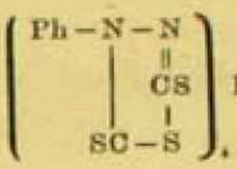
* The estimation throughout was effected by fusion with sodium nitrate and sodium carbonate.

A second preparation gave Pt = 25·32.



$$\left(\begin{array}{l} Ph-N-N \\ \quad\;\; | \quad\;\; \| \\ \quad\;\; | \quad\;\; CS \\ \quad\;\; | \quad\;\;\; | \\ \quad SC-S \end{array}\right)_4 Pt$$

requires, Pt = 17·73 ; S = 35·10.

It will thus be seen that here also the compound corresponding to the tetravalent platinum is never formed but a mixture of almost equal proportions of that yielded by trivalent and divalent platinum. As has been previously shown it is only in the case of the simple mercaptans like ethyl mercaptan that the products can be isolated in a pure state by taking proper precautions.

In the above reactions the free HCl of H_2PtCl_6 acting upon a portion of the potassium mercaptide, liberates the corresponding mercaptan, which is insoluble in water and the available chlorine atom of the tetravalent platinum chloride also acting upon potassium mercaptide gives rise to the disulphide equally insoluble. The dried precipitate was therefore exhausted first with alcohol and afterwards with benzene for the extraction of the impurities. The colour of the compound, which was yellow, after this treatment, became orange.

(c) *Phenyl-dithiobiazoline sulphydrate and cupric chloride.*

The potassium salt in aqueous solution was used as it was found to be more reactive than the mercaptan itself.

To a concentrated solution was added a dilute solution of cupric chloride with vigorous stirring. A gelatinuous precipitate was obtained which, when dried in a vacuum desiccator, was of a yellow colour. It was cupric mercaptide.

Result of Analysis.

0·1518 gave 0·247 CuO and 0·4002 $BaSO_4$.

Found	Calc. for $(PhN_2C_2S_3)_2Cu$.
Cu = 13·00	12·37
S = 36·21	37·39

Chlorine was proved to be absent.

By the reverse process, *i.e.* by using a dilute solution of the mercaptide and concentrated solution of cupric chloride, the corresponding chloro-mercaptide was obtained but it was contaminated with the mercaptide.

Found	Calc. for $(PhN_2C_2S_3)CuCl$.
Cu = 17·63	19·60
S = 30·66*	29·63
Cl = 6·28	10·96

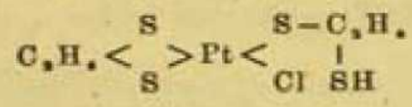
II

DIMERCAPTANS AND METALLIC HALIDES.

(a) Ethylene mercaptan (thioylycol) and platinic chloride.

A dilute alcoholic solution of platinic chloride is gradually added under vigorous stirring to a concentrated alcoholic solution of thioglycol. A yellowish brown precipitate is obtained, which is washed with alcohol and dried in a vacuum.

It conforms to the formula :



$$C_2H_4{<}\begin{matrix}S\\ \\ S\end{matrix}{>}Pt{<}\begin{matrix}S-C_2H_4\\ \quad\;\; | \\ Cl\quad SH\end{matrix}$$

It is evidently a remarkable compound ; two molecules of thioglycol which take part in the reaction have had three hydrogen atoms of the thiol-groups (SH) replaced by the three atoms of chlorine of platinic chloride and only one (SH) group remains intact. In orther words, it is three fourths a mercaptide and one fourth a chloride.

Result of Analysis.

0·0788 gave 0·0373 Pt, 0·032 AgCl and 0·1608 $BaSO_4$.

Found		Calc.
Pt	47·34	46·96
Cl	10·05	8·58
S	28·03	30·93

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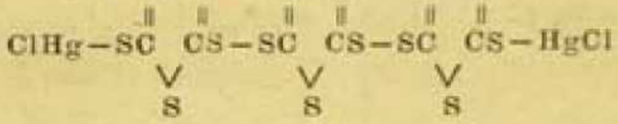
* The analysis was conducted by fusing the substance with sodium nitrate and sodium carbonate. Although the "melt" is evaporated with hydrochloric acid, it is not easy to convert the whole of the nitrate into the chloride and hence the p. c. of sulphur often comes out too high.

The compound is by no means pure; there is reason to conclude that a simpler mercaptide of the formula $C_2H_4<\begin{matrix}S\\ S\end{matrix}>Pt<\begin{matrix}Cl\\ Cl\end{matrix}$; (Pt = 54·39 Cl = 19·88 ; S = 17·91) is simultaneously formed in small quantities ; the higher value of platinum and chlorine and the lower value of sulphur is thus accounted for. Attempts to obtain the chloro-mercaptide in a purer form proved unsuccessful.

(*b*) *Thiobiazole-disulphydrate and mercuric chloride.*

An alcoholic solution of the di-mercaptan prepared according to the method of Busch (Ber., *27*, 2518) was added in a thin stream to an aqueous solution of mercuric chloride under vigorous stirring. A granular faintly yellow precipitate was obtained, which was sucked dry in the pump, washed with alcohol and dried in a vacuum over sulphuric acid. The compound conformed to the formula



i.e., it is the product of the condensation of three molecules of the di-mercaptan (Cf. similar chain compounds under the action of mercuric nitrite). Although no nitrous acid is present here to bring about oxidation, evidently so great is the tendency towards the formation of the chain compounds of sulphur that aerial oxidation suffices for the purpose.

Result of Analysis.

0·340 gave 0·154 Hg ; 0·1479 gave 0·328 $BaSO_4$.
0·1264 gave 10·20 c. c. N_2 at 29°c and 760 m. m. pressure.
0·1656 gave 0·0144 AgCl.

	Found	Calc. for $(C_2N_2S)^3S_6(HgCl)_2$.
Hg	45·29	43·65
S	30·45	31·48
N	8·95	9·18
Cl	6·05	7·76

The compound is seldom obtained pure ; products have sometimes been obtained in which only one molecule of the mercaptan takes part in the reaction ; they are, of course, contaminated with the above and vice-versâ.

	Found	Calc. for $(C_2N_2S)S_2(HgCl)_2$.
Hg	60·02	64·63
S	21·20	15·51
N	5·85	4·52
Cl	9·84	11·47

This preparation evidently contained an admixture of the previous one; the p.c. of mercury is thus lowered and that of sulphur increased.

(c) *Thiobiazole-disulphydrate and cupric chloride.*

To the concentrated solution of the potassium salt in dilute alcohol was added a dilute solution of cupric chloride. A yellow gelatinous compound was obtained, which was dried in a vacuum desiccator. It conformed to the formula $(N_2C_2S)S_2Cu+2H_2O$.

Result of Analysis.

0·2362 gave 0·0747 CuO and 0·6854 $BaSO_4$.

	Found	Calc.
Cu	25·26	25·66
S	39·85	38·79

By the reverse process *i.e.*, by using a concentrated solution of cupric chloride and a dilute solution of the mercaptide, an impure chloro-mercaptide was obtained.

	Found	Calc. for the corresponding chloro-mercaptide.
Cu	32·79	36·70
Cl	4·74	20·52

It will thus be seen that the tendency is always towards the formation of the mercaptide. As the series of mercaptides and chloro-mercaptides described above are insoluble in ordinary solvents, it is difficult to purify them.

III.

POTENTIAL MERCAPTANS AND METALLIC HALIDES.

(a) *Thiocarbamide and mercuric chloride.*

The components were acted upon both in alcoholic and in aqueous solution; a copious white precipitate was obtained which was washed with alcohol and dried in a vacuum. The filtrate was found to be neutral.

Result of Analysis.

0·2200 gave 0·1445 HgS; 0·1980 gave 0·1637 AgCl and 0·1446 $BaSO_4$.
0·1456 gave 10·4 c.c. N_2 at 22°c and at 760 m. m. pressure.
0·1313 gave 0·184 CO_2 and 0·0192 H_2O.

Found		Calc. for $CSN_2H_4HgCl_2$.
Hg	56·62	57·64
Cl	20·45	20·46
S	10·03	9·24
N	8·14	8·07
C	3·82	3·46
H	1·63	1·15

CONDUCTIVITY MEASUREMENT.

V	T	μ
256	21°·5	98·96

There were evidently two ions in solution and the dissociation is of the order of ammonium chloride.

(*b*) *Thiocarbamide and platinic chloride.*

An acetone solution of thiocarbamide was cautiously added under constant stirring to platinic chloride solution. An orange yellow precipitate was obtained which was washed with alcohol and dried in a vacuum.

Prep. 1. 0·0838 gave 0·0365 Pt, 0·0910 $BaSO_4$ and 0·0804 AgCl.
0·0582 gave 6·6 c. c. N_2 at 33°c and at 760 m. m. pressure.
Prep. 2. 0·0496 gave 0·0540 $BaSO_4$ and 0·0482 AgCl.

Found			Calc. for $C_2N_4H_7S_2Pt.Cl_3$.
	1	2	
Pt	43·56	——	45·01
S	14·91	14·95	14·17
Cl	23·74	24·03	23·57
N	12·39	——	12·40

(*c*) *Thiocarbamide and cupric chloride.*

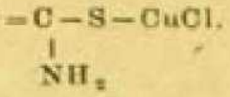
To an alcoholic solution of cupric chloride was added under constant stirring an alcoholic solution of the carbamide. The granular precipitate when dried in a vacuum had a white colour with a faintly bluish tint.

Result of Analysis.

0·0608 gave 0·9275 CuO.

0·0443 gave 6·2 c.c. N_2 at 31°c and 760 m. m. pressure.

9·0588 gave 0·0483 AgCl and 0·0780 $BaSO_4$.



	Found	Calc. for $NH=\underset{NH_2}{\underset{\mid}{C}}-S-CuCl$.
Cu	36·09	36·38
S	18·23	18·43
Cl	20·31	20·44
N	15·41	16·12

(a) *Thioacetamide and platinic chloride.*

Thioacetamide in alcoholic solution was added under stirring to platinic chloride solution and the precipitate which was brownish yellow, was treated as before.

Result of Analysis.

Prep. 1. 0·0524 gave 0·0222 Pt.
0·0856 gave 0·0782 AgCl.
Prep. 2. 0·0852 gave 0·0360 Pt and 0·0785 AgCl.
Prep. 3. 0·0334 gave 0·0144 Pt.
0·0813 gave 5·2 c.c. N_2 at 32°c and at 760 m. m. pressure.
Prep. 4. 0·1457 gave 0·0630 Pt; 0·1697 $BaSO_4$ and 0·1313 AgCl.

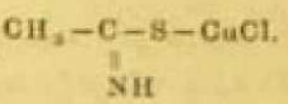
	Found				Calc. for $C_4H_9N_2S_2PtCl_3$.
	1	2	3	4	
Pt	42·40	42·26	43·11	43·83	43·20
S	——	——	——	15·99	14·23
Cl	22·59	22·79	——	22·29	23·68
N	——	——	7·01	——	6·23

(b) *Thioacetamide and cupric chloride.*

The method of preparation was exactly the same as in the preceding case; the colour of the salt was almost white. The alcoholic filtrate when distilled off was found to contain free hydrogen chloride.

Result of Analysis.

Prep. 1. 0·0555 gave 0·0250 CuO.
0·0595 gave 4·6 c.c. N_2 at 29·5°c and 760 m. m. pressure.
Prep. 2. 0·2818 gave 0·1261 CuO, 0·42 $BaSO_4$ and 0·2250 AgCl.

	Found		Calc. for  $CH_3-C(=NH)-S-CuCl$.
	1		
Cu	35·95	35·78	36·59
S	——	20·46	18·53
Cl	——	19·75	20·55
N	8·57	——	8·11

There can scarcely be any question as regards the purity of the compound analysed. The unusually high percentage of sulphur calls for an explanation. It was treated with CS_2 but no free sulphur could be detected. It is just possible that the free hydrogen chloride liberated, acts upon another portion of the thioacetamide and the latter undergoes the usual decomposition : H_2S and free sulphur being formed. The H_2S in turn would act upon the copper chloride forming copper sulphide and the free sulphur is probably adsorbed. This anomaly was only found in the case of thioacetamide.

(*a*) *Thiosemicarbazide and platinic chloride.*

On adding an aqueous solution* of semicarbazide to platinic chloride under varying conditions, dark brown crystalline precipitates were yielded but no definite formula could be assigned to any of these.

Result of Analysis.

	1	2	3	4
Pt	49·68	46·14	50·56	51·07
Cl	11·90	24·65	15·16	19·29
S	15·73	13·27	12·43	11·35
N	——	——	——	12·55

It will thus be seen that each of the above four preparations had a different composition ; evidently, mixtures were invariably obtained. After repeated failures the method as described below gave satisfactory result.

A concentrated aqueous solution of thiosemicarbazide was taken to which was added a dilute solution of platinic chloride. No immediate precipitation took place. In the course of half an hour a granular, hard, pale white crop began to be deposited. The solution was allowed to stand over-night. The granules when collected and dried had a yellowish white colour.

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* Thiosemicarbazide was found to be almost insoluble in cold alcohol, ether and acetone.

Result of Analysis.

0·2864 gave 0·1171 Pt, 0·1719 AgCl and 0·387 $BaSO_4$.
0·0381 gave 6·2 c.c. N_2 at 30° and 760 m. m. pressure.

	Found	Calc. for $PtCl_2S_3N_6H_4$.
Pt	40·89	40·04
S	18·56	19·78
Cl	14·85	14·63
N	17·97	17·31

Summary and conclusion.

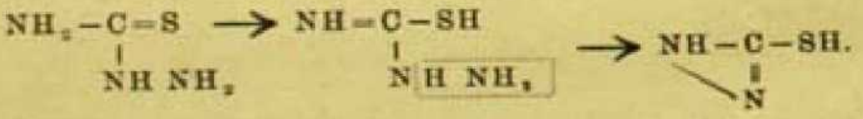
1. While mercuric chloride by interaction with a mercaptan yields invariably a chloro-mercaptide, thus:

$$RSH + ClHgCl = RSHgCl + HCl$$

cupric and platinic chlorides, on the other hand, have generally a tendency towards the formation of mercaptides or at best mercaptides with only a slight admixture of chloro-mercaptides.

2. Platinum in relation to mono-mercaptanic radicals either functions as trivalent or divalent.

3. The above chlorides bring about tautomeric changes in thiocarbamide and thioacetamide. Thiosemicarbazide also with platinic chloride undergoes similar transformation and yields a degradation product, which may be regarded as azomethylene-thiol:



$$\begin{array}{l} NH_2-C=S \\ \quad\;\; | \\ NH\,NH_2 \end{array} \longrightarrow \begin{array}{l} NH=C-SH \\ \quad\;\;\; | \\ N\boxed{H\,NH_2} \end{array} \longrightarrow NH-C-SH. \quad \searrow \overset{\|}{N}$$

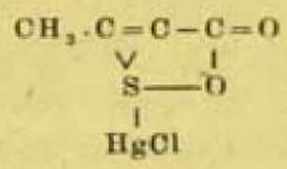
4. The chloro-mercaptides of the potential mercaptans, inasmuch as they contain one or more imino-groups, have the capacity to fix a molecule of hydrogen chloride; in fact, they are hydrochlorides of complex bases.

WANDERING OF HYDROGEN FROM THE ALPHA POSITION TO THE SULPHUR ATOM IN THIOPHENE AND THIOPHENE CARBOXYLIC ACIDS :

BY

PRAFULLA CHANDRA RÂY.

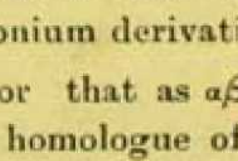
BY the interaction of $\alpha\beta$-thiocrotonic acid and mercuric chloride a compound was obtained to which was assigned the constitution as represented below :—



(Trans. Chem. Soc., 1917, *111*, 511)

It was evident that the elimination of an atom of chlorine as hydrochloric acid could only take place by the hydrogen of the carboxyl group shifting itself to the sulphur atom giving rise to a mercaptan and this latter in turn acting upon mercuric chloride in the usual way. The sulphur atom also now becomes tetravalent with the formation of a sulphonium derivative.

It occurred to the author that as $\alpha\beta$-thiocrotonic acid may be regarded as the lowermost homologue of α-thiophene carboxylic acid the latter should also yield with mercuric chloride a corresponding chloromercaptide. :

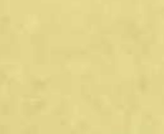


This anticipation has been fulfilled.

The wandering of the hydrogen of a carboxyl group to the nuclear atom in the ortho position is not without many parallels. In the case of orthoaldehydic acids, Liebermann has found that

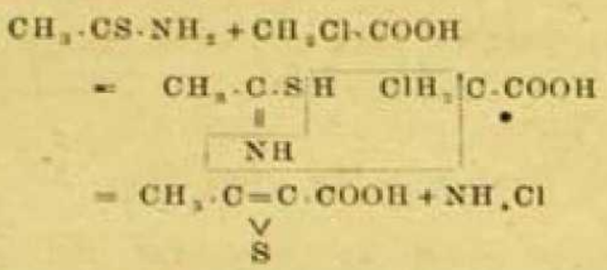
$$\begin{array}{l} \cdot C\cdot CHO \\ | \\ \cdot C\cdot COOH \end{array}$$

group changes to



(Ber., *19*, 765, 2288)

Peculiar interest attaches to the formation of the above chloromercuri-compound, when it is borne in mind that $\alpha\beta$-thiocrotonic acid is itself the product of a tautomeric change in its parent substance, namely thioacetamide thus :—

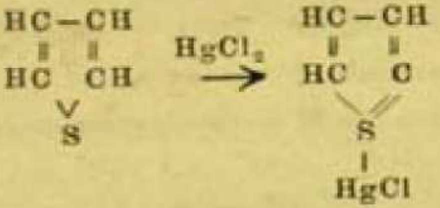


$$CH_3\cdot CS\cdot NH_2 + CH_2Cl\cdot COOH$$
$$= CH_3\cdot \underset{\underset{NH}{\|}}{C}\cdot SH \quad ClH_2C\cdot COOH$$
$$= CH_3\cdot \underset{\underset{S}{\vee}}{C=C}\cdot COOH + NH_4Cl$$

Volhard, however, has shewn that thiophene itself with mercuric chloride gives two mercuri chlorides of the formula C_4H_3SHgCl and $C_4H_2S\,(HgCl)_2$ respectively. He does not express any opinion as regards their constitution but simply contents himself by saying that it is the hydrogen in the α-position that is successively replaced by the chlorine of corrosive sublimate with the formation of hydrochloric acid (Ann. *267*, 172).

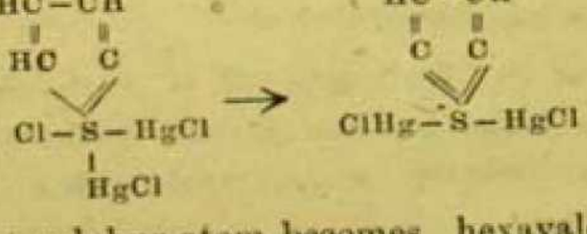
From the context one would gather that the HgCl groups remain attached to the two neighbouring carbon atoms.

The mechanism of the reaction on the present instance is easily intelligible on the hypothesis that thiophene acts as a potential mercaptan in the presence of suitable reagents, e.g. $HgCl_2$, thus



the divalent sulphur atom becoming tetravalent.

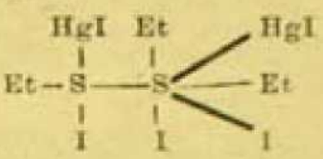
When, however, a second molecule of mercuric chloride acts upon the above, a compound of this formula is momentarily formed.



i.e., the tetravalent sulphur atom becomes hexavalent, but as this configuration is unstable, a molecule of hydrogen chloride goes off and a dimercuri-chloride is generated. It is equally possible that by the further action of $HgCl_2$ the tetravalent sulphur atom becomes hexavalent by the wandering of the second labile dydrogen in the α-position giving rise to a mercaptan and consequently to a chloromercaptide. The author has recently succeeded in preparing a compound, which has the empirical formula

$$[Et_2S_2, HgI_2, EtI]HgI_2^*$$

i.e., ethyldisulphonium-mercuri-iodide (Trans. Chem. Soc., 1916, *109*, 135) in combination with an additional molecule of HgI_2. It may be represented by the graphic formula



In other words, one atom of sulphur in the chain behaves as tetravalent and the other as hexavalent.

Volhard also noticed that α-methyl thiophene gives only one monomercurichloride ; this is readily explained as the adjacent labile hydrogen being already replaced by the CH_3 group is no longer available for combination with the chlorine atom.

One strong argument in favour of the constitution suggested above is based upon the strong affinity of sulphur for the HgCl group, which justifies the very nomenclature of mercaptans. It is scarcely possible that the HgCl radical would be linked to the carbon atom in preference to the sulphur atom. For, in that case the hydrogen in the β-position might equally have been replaced ; moreover, benzene might also have been expected to have one or more of its hydrogen atoms replaced by (HgCl).

EXPERIMENTAL.

Thiophene α-carboxylic acid was prepared according to the method of Paal and Tafel (Ber., *18*, 458). The aqueous solution when treated with a solution of mercuric chloride gave a white gelatinous precipitate, which was dried in a vacuum over sulphuric acid.

Result of analysis :—

0.0625 gave 0.0247 AgCl and 0.038 $BaSO_4$.

0.248 gave 0.1574 HgS.

	Found	Calc. for $C_5H_3O_2SHgCl$
Hg	54.69	55.17
Cl	9.77	9.79
S	8.35	8.83

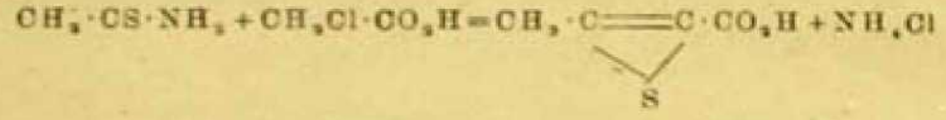
---

* Details of this interesting compound will be comunicated later on.

SYNTHESIS OF αβ-THIOCROTONIC ACID.

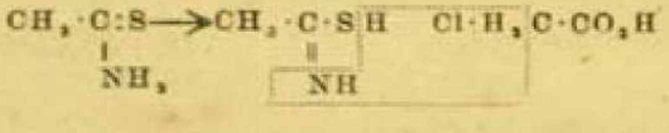
By Prafulla Chandra Rây and Manik Lal Dey.

Monochloroacetic acid and thioacetamide have been found to interact in acetone solution with the production of *αβ-thiocrotonic acid* according to the following equation :



$$CH_3\cdot CS\cdot NH_2+CH_2Cl\cdot CO_2H=CH_3\cdot \underset{S}{C{=\!=}C}\cdot CO_2H+NH_4Cl$$

Evidently the thio-body undergoes a tautomeric change thus :



$$CH_3\cdot\underset{NH_2}{\underset{|}{C}}{:}S\longrightarrow CH_3\cdot\underset{NH}{\underset{\|}{C}}\cdot S\boxed{H\quad Cl\cdot H_2}C\cdot CO_2H$$

Experimental.

Molecular proportions of thioacetamide and monochloroacetic acid are separately dissolved in the minimum quantity of anhydrous acetone, the solution mixed and set aside. In the course of twenty-four hours a precipitate of ammonium chloride is noticed, which increases day by day, and after about a week the ammonium chloride is filtered off.

The filtrate is now freed from acetone by evaporation at the ordinary temparature when a heavy, orange-yellow oil of an unpleasant odour remains with a few crystals of ammonium chloride. The oil is dissolved in ether, the solution filtered and evaporated, and the oil allowed to crystallise in a desiccator.

It takes about three months to obtain a good crop of crystals, but occasionally they appear earlier. The crystals are purified by recrystallisation, first from acetone and then from alcohol. The first crop of crystals obtained in this way were pure, had a faint yellow tint, and melted sharply at 135°; when the ethereal solution was evaporated slowly, transparent, rhombic plates were obtained.

The acid is fairly soluble in water, readily so in alcohol, acetone, or ether, and sparingly so in chloroform. Its solution rapidly decolorises bromine water and alkaline permanganate solution, thus proving its unsaturated character.

The *barium* salt forms shining, rhombic plates, the *lead* salt white, needle-shaped crystals, and the *silver* salt is obtained as a faintly yellow, gelatinous precipitate.

Attempts to analyse the acid met with no success; thus when mixed with concentrated nitric acid in a sealed tube for the purpose of estimating sulphur, it explodes violently. Fusion with sodium carbonate and nitrate is also attended with explosion. The barium, silver and lead salts were therefore analysed.

Barium salt :

0·1238 gave 0·0800 $BaSO_4$. $Ba = 37{\cdot}99$.
0·1118 ,, 0·1460 $BaSO_4$. $S = 17{\cdot}94$.

$C_8H_6O_4S_2Ba$ requires $Ba = 37{\cdot}23$; $S = 17{\cdot}44$ per cent.

Lead salt :

0·1682 gave 0·1368 CO_2 and 0·0514 H_2O. $C = 22{\cdot}10$; $H = 3{\cdot}40$.*
0·0628 ,, 0·0432 $PbSO_4$. $Pb = 46{\cdot}97$.

	Found	Calc. for $C_8H_6O_4S_2Pb$.
Pb	... 46·97	47·17
C	... 22·10	22·05
H*	... 3·40	1·38

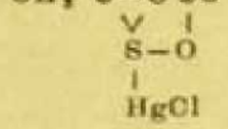
Silver salt :

0·1250 gave 0·0610 Ag. $Ag = 48{\cdot}80$.

$C_4H_5O_2SAg$ requires $Ag = 48{\cdot}43$ per cent.

The formula of the compound is thus fully established.

Mercury salt.—With mercuric chloride the acid forms a compound containing an atom of chlorine, to which the constitutional formula



$$\begin{array}{c} CH_3\cdot C{=}C\cdot CO \\ \vee \quad | \\ S{-}O \\ | \\ HgCl \end{array}$$

must be assigned.

Here evidently a wandering of the hydrogen of the carboxyl to the sulphur atom takes place, a *mercaptan* being formed.

I. 0·0790 gave 0·0524 HgS. $Hg = 57{\cdot}17$.
II. 0·0828 ,, 0·0553 HgS. $Hg = 57{\cdot}57$.
0·0920 ,, 0·0620 $BaSO_4$. $S = 9{\cdot}26$.
0·0812 ,, 0·0339 AgCl. $Cl = 10{\cdot}24$.

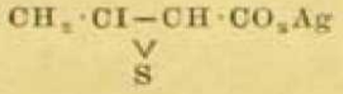
$C_4H_5O_2ClSHg$ requires $Hg = 57{\cdot}06$; $S = 9{\cdot}13$; $Cl = 10{\cdot}13$ per cent.

---

* Several samples of organic mercury compounds had been previously analysed in the combustion tube and hence traces of mercury vapour were carried into the calcium chloride tube, which increased the apparent percentage of hydrogen.

Action of Hydriodic Acid.

The concentrated aqueous solution of the acid was repeatedly treated with concentrated hydriodic acid and evaporated to dryness on the water-bath so as completely to remove every trace of the free halogen acid. The residue was dissolved in water, and on treatment with silver nitrate solution it gave a copious, pale yellow precipitate of *silver β-iodo-αβ-thiobutyrate*:



$$\underbrace{CH_2\cdot CI-CH}_{S}\cdot CO_2Ag$$

0·0256 gave 0·0174 AgI.* $Ag=31\cdot23$; $I=36\cdot73$.

$C_4H_4O_2ISAg$ requires $Ag=30\cdot77$; $I=36\cdot18$ per cent.

Molecular Conductivity and Dissociation Constant.

The conductivity of the acid and of its barium salt at different dilutions was determined. The dissociation constant of the acid and the degree of dissociation of the salt were calculated from the data.

Acid. $t=24°$.			*Barium Salt.* $t=25\cdot3°$.		
v in litres.	μ (equivalent conductivity).	K.	v	μ (equivalent conductivity).	a
60	42·6	0·000020	200	94	0·75
120	58	0·000019	600	102	0·81
240	77	0·000018	1,200	108	0·86
480	101	0·000017	2,200	117	0·93
960	132	0·000016	4,200	122	0·97
∞	410 mean	0·000018	10,200	126	1·00

K for crotonic acid = 0·000002 ; as a general rule, the substitution of sulphur for hydrogen in organic acids increases the dissociation constant. Thus, in the present instance the value of K for the thio-compound is considerably higher.

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* By Carius's method, without addition of silver nitrate

INTERACTION OF THE POTASSIUM SALTS OF PHENYL-DITHIO-BIAZOLINE-SULPHYDRATE AND THIO-BIAZOLE-DISULPHYDRATE WITH THE HALOGENATED ORGANIC COMPOUNDS.

BY

PRAFULLA CHANDRA RÂY

PRAFULLA CHANDRA GUHA

AND RADHA KISHEN DAS.

Gabriel and, later on, Holmberg treated sodium ethylmercaptide with chloroform and obtained orthotrithioformic-ethylester $CH(SEt)_3$ (Ber., *10*, 185, Ibid *40*, 1740)—a compound which is the sulphur analogue of Williamson and Kay's ether. In the present investigation it will be shown that the potassium atom of the complex cyclic mercaptides named above is singularly reactive towards the halogen atoms of the organic bodies of divers types. Thus, chloroform, bromoform and iodoform yield compounds with the potassium monomercaptide, which may be represented by the general equation given below :—

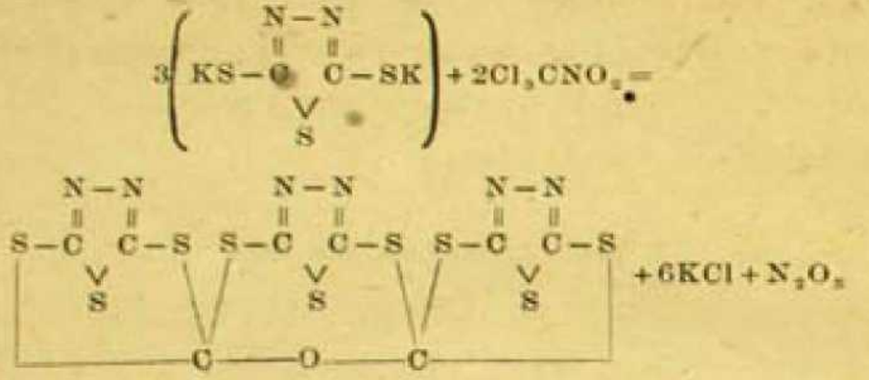
$$3K\text{-}Biaz + CHX_3 = 3KX + CH(Biaz)_3$$

where X represents an halogen atom and "Biaz" the radicle of the complex mercaptide. Nitro-chloroform acts exactly like chloroform but is far more reactive than the latter and the reaction may be expressed by the following equation :—

$$3Biaz\text{-}K + Cl_3CNO_2 = NO_2C(Biaz)_3 + 3KCl.$$

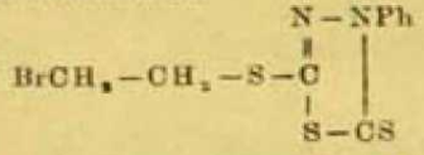
The behaviour of tribromoresorcin, benzal-chloride, monochloro acetic acid and ethylene dibromide has also been found to be of identical nature. The potassium salt of thiobiazole-disulphydrate, on the other hand, acts almost as an inert substance towards chloro-, bromo-, and iodoform.

It is evident that the presence of two (SK) groups of the dimercaptide exercises a sort of inhibitory influence on the halogen atoms. The reactivity of these halogenated bodies can be, however, materially enhanced by further substituting the remaining hydrogen atom by a nitro-group. For instance, nitro-chloroform very readily acts upon the dimercaptide even in the cold. The introduction of an additional negative group has thus a marked effect. The reaction may be represented as follows :—



Nitrous fumes (N_2O_3) escape during the reaction and an atom of oxygen as shown above forms the connecting link between the two carbon atoms of the residues of two molecules of nitrochloroform.

Ethylene-dibromide reacts upon the potassium mono-mercaptide, but only one atom of bromine is acted upon by the potassium atom resulting in the formation of



Monochloro acetic acid, benzal-chloride and ethylene dibromide, no doubt, act upon the dimercaptide but the products of the reaction have been found to be insoluble in the ordinary solvents and thus cannot be purified.

EXPERIMENTAL.

K-Biaz with iodoform, bromoform and chloroform.*

The reacting substances were taken in molecular proportions, *i.e.* 3 molecules of the mercaptide were treated with one molecule of the halogenated body in alcoholic solution. The reaction mixture was refluxed on the water bath for several hours. An insoluble mass was obtained consisting of the potassium halide and the organic derivative. The mixture was then triturated in a mortar with water. The aqueous filtrate, on evaporation, gave crystals of the potassium

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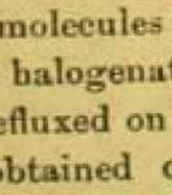
* For brevity's sake "Biaz" has been used for (R-S) where R is the complex radicle



halide. The insoluble portion was dried and dissolved in benzene; on evaporation of the solvent, an oily liquid was obtained. It was redissolved in benzene and precipitated by alcohol as an oil. On keeping, the oil turned into a yellow powder. As it was difficult to get rid of the last trace of iodoform, the powder was repeatedly washed with alcohol and dried in the steam oven, till the odour of iodoform was no longer perceptible. The substance had the melting point 66-68°.

With bromoform exactly the same method was followed. But as it is highly volatile, the excess of it was easily removed from the yellow compound, which had the melting point 66-68°.

When the reaction mixture in alcoholic solution was heated to 210-220° in a sealed tube for several hours, a tarry resinous mass was obtained; it was filtered off the mother liquor and dissolved in benzene. Addition of alcohol to the benzene solution gave the same tarry precipitate but not the yellow powder. The alcoholic mother liquor, on concentration, gave needle-shaped shining crystals which had the sharp melting point 62°. Analysis proved this product to be the alcoholate of the compound described above, conforming to the formula $CH(Biaz)_3 + 2C_2H_5OH$. The yield of the crystalline product was very poor, evidently most part of the product had become resinified owing to the high temperature employed.

No reaction took place when chloroform was refluxed with the mercaptide in alcoholic solution. The mixture was therefore heated in a sealed tube as in the case of bromoform. The filtrate, separated from the resinified mass, gave, on evaporation, crystals of the alcoholate having the melting point 62°.

It is thus evident, that iodoform and bromoform are more reactive towards the mercaptide than chloroform.

Result of analysis :—

(1) The yellow powder from iodoform, m.p. 66-68°.

0·0953 gave 0·1502 CO_2 and 0·0202 H_2O.

0·0876 gave 0·2087 $BaSO_4$

0·075 gave 8.3 c. c. N_2 at 24° and 760 m. m. pressure.

Found	Calc. for $CH(Biaz)_3$
C 42·98	43·60
H 2·33	2·76
S 41·19	41·80
N 12·50	12·21

The yellow powder from bromoform gave C=43·1, H=2·93; N=12·59.

The alcoholate :

Result of analysis :—

0·1520 gave 0·2532 CO_2
0·1101 gave 11·4 c.c. N_2 at 32° and 760 m.m. pressure
0·1260 gave 0·3532 $BaSO_4$.

Found	Calc. for $CH(Biaz)_3+2C_2H_5OH$
C 45·23	44·6
N 11·26	10·85
S 38·48*	37·50

K-Biaz and Nitro-chloroform.

The alcoholic solution of the parent substances was refluxed as before. A bulky yellow precipitate was obtained; after decanting off the mother liquor it was washed with alcohol and triturated with water in a mortar to remove the potassium chloride. It was obtained pure by crystallising from hot benzene. Yellow shining crystals were obtained; melting point 128-129°. The reaction was almost quantitative as was proved by weighing the potassium chloride formed.

Result of analysis :—

0·1140 gave 0·1727 CO_2 and 0·0307 H_2O.
0·0948 gave 11·4 c. c. N_2 at 32° and 760 m. m. pressure.

Found	Calc. for $NO_2C\ (Biaz)_3$
C 41·31	41·97
N 13·18	13·37

K-Biaz and tribromoresorcinol.

The alcoholic solution of the parent substances was refluxed as before. The amorphous powder, obtained after the reaction, was freed from potassium bromide by water and was dried. It was dissolved in a mixture of alcohol and carbon bisulphide; on evaporation, shining crystals melting at 166° were obtained.

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* It may be necessary to point out that in these compounds, the sulphur atom is linked both to a fatty as also to an aromatic and cyclic residue. Carius' method gave the result unusually low owing to the formation of sulphonic acid. The excess of nitric acid was, therefore, neutralised with sodium carbonate and evaporated to dryness and fused in a silver dish. The "melt" was several times evaporated with hydrochloric acid before the addition of barium chloride. Owing to the presence of a large amount of sodium chloride and unacted upon sodium nitrate, the result generally comes out a little high.

Result of analysis :—

0·0881 gave 0·1458 CO_2 and 0·0236 H_2O.

0·0724 gave 0·1897 $BaSO_4$.

Found		Calc. for $(OH)_2C_6H(Biaz)_3$.
C	45·13	46·03
H	2·97	2·30
S	36·00	36·55

K-Biaz and Benzal-chloride.

The components in alcoholic solution were refluxed for about an hour. The crystalline product had the melting point 59-62°.

Result of analysis :—

0·0708 gave 0·1321 CO_2 and 0·0193 H_2O

0·0849 gave 8·6 c. c. N_2 at 22° and 760 m. m. pressure.

0·0974 gave 0·2550 $BaSO_4$.

Found		Calc. for $C_6H_5CH(Biaz)_2$
C	50·87	51·11
H	3·03	2·96
N	11·02	10·40
S	35·83	35·55

K-Biaz and Ethylene dibromide.

After refluxing in alcoholic solution as usual the insoluble product was freed from potassium bromide by means of water and dried. This was then dissolved in ether. On evaporation, shining crystals melting at 94° began to appear.

Result of analysis :—

0·1644 gave 0·2183 CO_2

0·0812 gave 6·6 c.c. N_2 at 30° and 760 m.m. pressure.

0·1303 gave 0·0715 AgBr

Found		Calc. for $BrCH_2CH_2(Biaz)$.
C	36·21	36·03
N	8·97	8·40
Br	23·35	24·02

K-Biaz and Monochloro acetic acid.

The reaction takes place even in the cold on mixing up the components in aqueous solution and is completed on heating. The product crystallises out from boiling water in silky needles of melting point 145°.

Result of analysis :—

0.1279 gave 0·1935 CO_2 and 0·0414 H_2O

0·1580 gave 0·3495 $BaSO_4$

0·1697 gave 15·00 c.c. N_2 at 24° and 760 m.m. pressure.

	Found	Calc. for $CO_2HCH_2(Biaz)$.
C	41·26	42·06
H	3·60	2·81
N	9·99	9·86
S	30·38*	33·81

It is of interest to note that while monochloroacetic acid behaves like an ordinary chlorinated body, dichlor-, and trichlor-acetic-acids, on the other hand, behave like "strong acids" such as hydrochloric acid ; *i.e.* they simply reproduce the original mercaptan.

Potassium salt of thiobiazoledisulphydrate and nitro-chloroform.

The components were refluxed with alcohol for several hours. After some time, nitrous fumes were evolved and a yellow precipitate was obtained. On cooling, it was filtered off the mother liquor and washed with alcohol to remove the adhering nitrochloroform. The powder was triturated in a mortar with water to remove the potassium chloride formed during the reaction. The yellow powder was found to be insoluble in nearly a dozen of ordinary solvents and even in mixtures of some of these. Two different preparations had, however, the same melting point (166-168°) and the same percentage composition.

Result of analysis :—

0·1734 gave 0·1274 CO_2

0·0853 gave 14·00 c.c. N_2 at 31° and 760 m.m. pressure.

0·0899 gave 0·3907 $BaSO_4$.

	Found	Calc. for $(C_2N_2S_3)_3C_2O$.
C	20·04	19·83
N	18·03	17·40
S	59·68	59·50

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* For explanation of the low result of sulphur, see foot note ante p. 52.

Mercuri-Sulphoxy Chloride.

Chain Compounds of Sulphur.

Part V.

BY

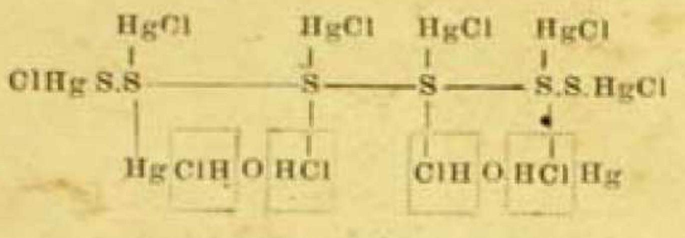
Prafulla Chandra Rây.

The close analogy between mercuric chloride and nitrite has been found to hold good throughout the investigations carried on from 1918 onwards. Thus, whilst mercuric *nitrate* with sodium sulphate at once gives an abundant yellow precipitate of the oxysulphate, known as the *turpeth mineral*—the chloride and the nitrite fail to give it. (Trans. Chem. Soc. 1897, 1103). The explanation lies in the fact that these latter salts are very feebly ionised in solution and thus have no tendency to yield basic compounds. Ammonia, amines and even a class of alkaloids have been found to behave towards mercuric nitrite similar to the chlorides (Trans. 1913, *103*, 3; Trans. 1917, *111*, 507).

The substituted thiocarbamides, thiocarbimides, thiobenzamide etc., have been shown to give rise to a purely inorganic sulphoxynitrite of the empirical formula $[3(SHgNO_2)HgO]_2$, which is in reality a chain compound containing six atoms of sulphur in the link (Trans. 1917, *111*, 104).

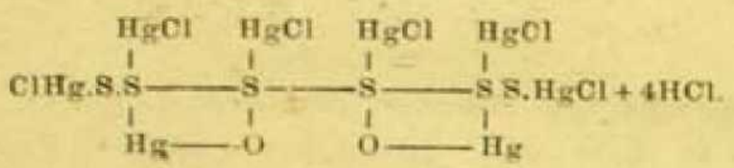
Recently, an attempt was made to isolate the radicle $(SHgCl)_2$, which would be the analogue of mercuri-iodo-sulphide $(SHgI)_2$ l.c. 109, by treating mercuric chloride with some typical thiobodies named above, as also thioacetic acid and ammonium dithiocarbamate. It was expected that in each case the radical (SHgCl) would get detached from the parent body and lead an independent existence. This expectation has been realised, but in a qualified sense. The radical SHgCl, no sooner it separates out, assumes the from $[3(SHgCl)HgO]_2$, which is the exact analogue of the oxy-nitrite. It has been shown already that the complex nitrite containing several NO_2 groups by the elimination of N_2O_3 (i.e. $NO+NO_2$) readily yields the oxy-nitrite.

At the first sight, it is not easy to understand how the chloride also would give birth to an oxy-salt. The explanation lies ready at hand when it is borne in mind that here water takes part in the reaction; $[3(SHgCl)\ HgO]_2$ is formed thus:



$$\begin{array}{cccccccc} & HgCl & & HgCl & & HgCl & & HgCl \\ ClHg\ S. & S & — & S & — & S & — & S.S.HgCl \\ & Hg\ ClH & O & HCl & & ClH & O & HCl\ Hg \end{array}$$

i.e.,



$$\begin{array}{cccccccc} & HgCl & & HgCl & & HgCl & & HgCl \\ ClHg.S. & S & — & S & — & S & — & S\ S.HgCl + 4HCl \\ & Hg & — & O & & O & — & Hg \end{array}$$

In other words, as soon as the radicle SHgCl separates out every three of this take up an additional molecule of mercuric chloride, *i.e.*, the radicles HgCl and Cl and a molecule of water simultaneously takes part in the reaction, four molecules of hydrochloric acid are generated and the oxygen atom forms the connecting link between the mercury atom and the neighbouring sulphur atom and the two symmetrical complexes coalesce into a single molecule.

It is necessary to point out here that whilst the radicle $SHgNO_2$ has often a tendency to part company with the parent body, the radicle SHgCl often prefers, on the other hand, to remain attached to it. Thus, thiocarbamide when acted upon by mercuric chloride yields the compound $(NH_2{-}C{:}NH{-}SHgCl)\ HCl$, which is actually a *hydrochloride* as has been shown in a previous communication. If, however, thiocarbamide be converted into its diacetyl derivative and then treated with mercuric chloride, the molecule undergoes a break up with the detachment of the radicle SHgCl and formation of the oxychloride; *S*-diphenythiocarbamide also behaves similary.* Evidently, the introduction of the negative radicles acetyl and phenyl neutralises the basic character of the compound due to the presence of an amino- and imino group and deprives it of the power of the formation of a hydrochloride in which character alone it is stable.

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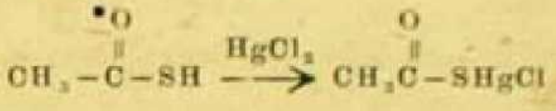
* P. K. Sen working in this laboratory has prepared diacetyl thiocarbamide and has already shown that both this compound and s-diphenyl thiocabamide yield with mercuric chloride the oxy-chloride $[3(SHgCl)HgO]_2$.

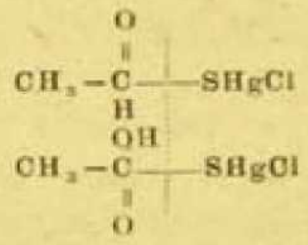
It is a characterestic property of mercaptans, real and potential, that with mercuric nitrite and chloride they yield the nitrite mercaptide and chloro-mercaptide respectively. Thioacetic acid, though an acid, contains the group SH and as such behaves like a typical mercaptan.

Thus :



$$CH_3-\overset{\overset{O}{\|}}{C}-SH \xrightarrow{HgCl_2} CH_3\overset{\overset{O}{\|}}{C}-SHgCl$$

As soon as this compound is formed it acts upon a molecule of water.



$$\begin{array}{l} CH_3-\overset{\overset{O}{\|}}{C}-SHgCl \\ \quad\;\; H \\ \quad\;\; OH \\ CH_3-\underset{\underset{O}{\|}}{C}-SHgCl \end{array}$$

and the scission takes place as shown by the dotted line, a molecule of acetaldehyde and acetic acid being formed.

Ammonium dithiocarbamate assumes the tautomeric form $NH=C<^{SNH_4}_{SH}$ both the radicles -SH and -SNH$_4$ with mercuric chloride yield -SHgCl, which separates out and assumes the oxychloride form.

Allyl thiocarbimide $C_3H_5N:C:S$ simply takes on the components of mercuric chloride and $C_3H_5N:C:SCl\text{-}HgCl$ is temporarily formed, the sulphur atom becoming tetravalent. As this configuration is unstable, a rupture takes place along the line of least resistance, the radicle $=S<^{Cl}_{HgCl}$ decomposes into the stable radicle -SHgCl and chlorine; whilst the organic portion of the complex RN:C< with a molecule of water yields a primary amine and carbon monoxide.

Experimental.

Method of preparation :—The thio-body in aqueous or alcoholic solution as the case may be was added by means of a pipette in a thin stream to an aqueous solution of mercuric chloride under vigorous stirring, care being taken that the latter was always in large excess.

A granular white preocipitate was obtained which was washed first with water and then with alcohol and finally dried in a vacuum over sulphuric acid. A special precaution is necessary in the case of mustard oil. If an alcoholic solution of it is added to an aqueous solution of mercuric chloride the white precipitate is obtained, but, at the same time heavy oily globules begin to settle down at the bottom and it is not always easy to separate them from the sulphoxy-chloride. It is best to add the alcoholic solution of the mustard oil to an alcoholic solution of mercuric chloride. The mixture remains clear but on copious dilution with water and stirring, the white precipitate begins to put in an appearance. The reaction mixture is allowed to stand over night and the product collected and treated as before.

The interaction of each of the above mentioned thio-bodies with mercuric chloride was repeated several times and the composition throughout was found to be identical. It is therefore not necessary to give the analysis of each preparation ; that of one or two typical ones are given below.

Mercuric chloride and thioacetic acid.

Result of analysis :—

0·2587 gave 0·2370 HgS ;

0·1465 gave 0·0625 AgCl and 0·1070 $BaSO_4$ by fusion with $NaNO_3$ and Na_2CO_3.

	Found	Calc for $Hg_4S_3Cl_3O$
Hg	78·98	78·58
Cl	10·55	10·46
S	10·03	9·43

Mercuric Chloride and mustard oil.

Result of analysis :—

0·3402 gave by distillation with copper powder 0·2631 Hg.

0·2795 gave 0·1285 AgCl and 0·1818 $BsSO_4$.

Found :—Hg = 77·34 ; Cl = 11·37 ; S = 8·93.

The absence of carbon was shown by combustion analysis.

Mercury Mercaptide Nitrites and their Reaction with the Alykyl Iodides. Part VI. Chain Compounds of Sulphur—*contd.*

BY

Prafulla Chandra Rây

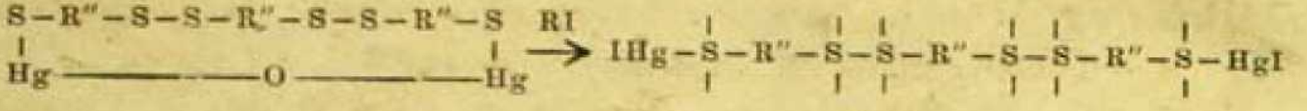
AND

Prafulla Chândra Guha.

In part IV of the present series of investigations, it has been shown that thiobiazole disulphydrate gives by interacting with mercuric nitrite a series of sulphoxy compounds in which two, three and four molecules respectively, of the dimercaptan are condensed. In the present investigation, the polysulphonium (viz. tetra-, hexa-, octa-, and dodeca) compounds will mainly be dealt with, which are formed by the action of alkyl iodides upon these sulphoxy compounds as also upon a new hexanuclear sulphoxy one, formed by the condensation of six molecules of the dimercaptan.

The sulphoxy bodies may be included under the general formula $(C_2N_2S_3)\ xHg_2O$; where $x=2, 3, 4$ or 6. A condensation product of five molecules has not as yet been obtained. It is not easy to explain why in one operation the value of x should be two and in others it should run up to six; possibly the concentration of the parent substances is the main determining factor. It has often been found that two preparations under similar conditions had identical composition. In the majority of cases the value of x has been found to be three occasionally two and four, and only rarely six.

The preparations could not have been admixtures because, each of them strictly conformed to a definite formula. But the must convincing proof of these compounds being of definite composion is afforded by their deportment towards the alkyl iodides. These sulphoxy bodies behave exactly like mercaptide nitrites and yield, as a rule, the corresponding sulphonium derivatives and in a few cases those with a fewer number of nuclei. The reducing action of the alkyl iodide removes the oxyen atom of the sulphoxy ring and the bonds being thus snapped, an open chain compound is formed ; thus :

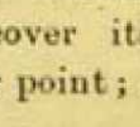


$$\underset{Hg\text{————————}O\text{————————}Hg}{S-R''-S-S-R''-S-S-R''-S}\quad RI \longrightarrow IHg-\overset{|}{\underset{|}{S}}-R''-\overset{|}{\underset{|}{S}}-\overset{|}{\underset{|}{S}}-R''-\overset{|}{\underset{|}{S}}-\overset{|}{\underset{|}{S}}-R''-\overset{|}{\underset{|}{S}}-HgI$$

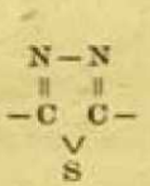
The six sulphur atoms of the chain now become quadrivalent by taking up the components of alkyl iodide.

In this manner, a series of tetra—, hexa—, octa— and dodeca-sulphonium compounds have been prepared. Each of these with the exception of propyl and butyl derivatives is characterised by its crystalline character and moreover its successive crops have been found to have the same melting point ; the possibility of their being mixtures is thus precluded.

Another interesting point is the shifting of the double bonds ; thus :

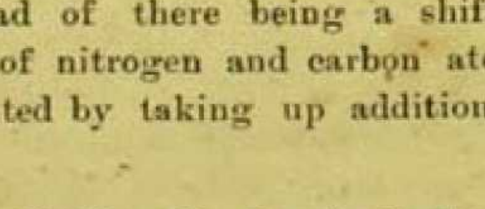


takes up two alkyl radicles and is changed into

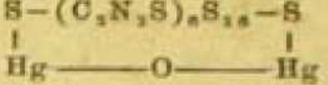


where R = Me, Et, Pr, Bu. As a rule, this is confined only to one nucleus. Evidently we have here an extension of Thiele's theory to nitrogen compounds.

In one isolated instance and that in the case of interaction with methyl iodide, instead of there being a shifting of the double bonds, both the pairs of nitrogen and carbon atoms throughout the molecule were saturated by taking up additional methyl radicles ; thus :



EXPERIMENTAL.

Hexanuclear sulphoxy compound 
$$\begin{array}{ccc} S-(C_2N_2S)_6S_{12} & - & S \\ | & & | \\ Hg & -O- & Hg \end{array}$$

The compound was associated with 7 H_2O·

0·1236 gave 0·049 HgS. Hg=28·52

0·1109 „ 0·3215 $BaSO_4$. S=39·82

0·1715 „ 18 c.c. N_2 at 30° and 780 mm. N=11·59

Theory requires, Hg=27·97 ; S=40·28 ; N=11·75

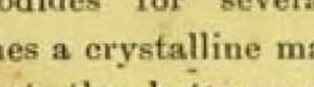
II

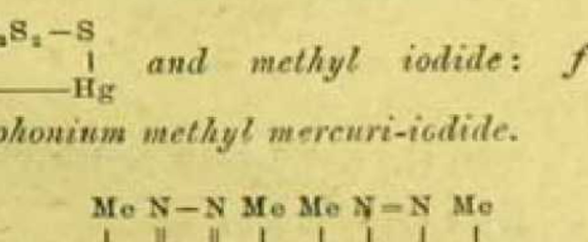
INTERACTION WITH THE ALKYL IODIDES.

General method of preparation :

The above sulphoxy derivatives were refluxed on a water bath with alkyl iodides for several hours and allowed to stand overnight, sometimes a crystalline mass and sometimes a heavy dark brown oil settled at the bottom ; the excess of alkyl iodide was decanted or boiled off and the former dissolved in the minimum quantity of acetone and filtered off from the insoluble matter whenever necessary. On adding ether to the filtrate, a pale yellow, mealy crystalline precipitate was obtained. This process was repeated to further purify the product.

BINUCLEAR CONDENSATION.

(1) 
$$\begin{array}{ccc} S-(C_2N_2S)_2S_2 & - & S \\ | & & | \\ Hg & -O- & Hg \end{array}$$
and methyl iodide: formation of Dithiobiazole tetrasulphonium methyl mercuri-iodide.



The product had the m.p. 101-102°

0·2186 gave 0·0567 Hg and 0·1971 AgI. Hg=25·94 ; I=49·23

0·1610 „ 0·0480 CO_2. C=7·75

$C_{10}H_{18}N_4S_6Hg_2I_6$ requires Hg=25·84 ; I=49·33 ; C=8·13

(2) The corresponding ethyl iodide compound was sparingly soluble in acetone and was therefore purified by crystallisation from the boiling solvent, m.p. 107°

Prep. I

0·2674 gave 0·0647 Hg and 0·2138 AgI. Hg=24·19; I=43·2[*]

0·2343 „ 0·0967 CO_2. C=11·25

0·2049 „ 6·4 c.c. N_2 at 24° and 760 mm. N=3·53

Prep. II

0·3600 gave 0·0885 Hg and 0·1232 gave 0·0516 CO_2.
Hg=24·58; C=11·42

$C_{16}H_{30}N_4S_6Hg_2I_6$ requires, Hg=24·51; I=46·69; C=11·76;
N=3·43[†]

The corresponding binuclear tetrasulphonium compound with n. propyl and n. butyl iodides did not yield crystalline products, but only a dark brown treacle-like pasty mass, which was purified by repeated precipitation by ether from acetone solution. It has already been shown that with the simpler mercaptides, these higher n. alkyl iodides gave crystalline products with sharp m.p. (Cf. T. 1916, *109*, 606). It is very likely that in these particular cases the alkyl radicles are converted into the iso-varieties, from the consideration that isoalkyl iodides always gave such pasty masses (l.c. 607).

(3) *The corresponding tetrasulphonium propyl compound:*

0·3407 gave 0·0814 Hg and 0·2821 AgI. Hg=23·89; I=44.74

0·2271 „ 0·1170 CO_2. C=14·05

$C_{22}H_{42}N_4S_6Hg_2I_6$ requires Hg=23·31; I=44·40; C=15·38

(4) The butyl compound:

0·3675 gave 0·0800 Hg and 0·2839 AgI. Hg=21·77; I=4175

0·1973 „ 0·1278 CO_2. C=17·66

0·1280 „ 3·6 c.c. N_2 at 30° and 760 mm. N=3·11

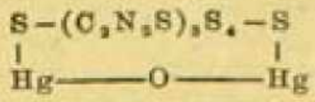
$C_{28}H_{54}N_4S_6Hg_2I_6$ requires Hg=22·22; I=42·33; C=18·60;
N=3·11

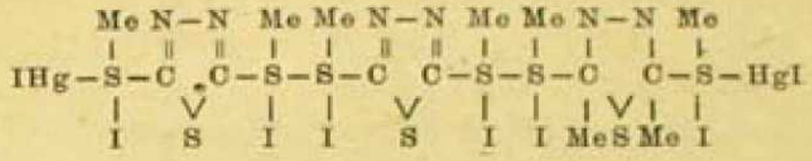
---

[*] As a large quantity of copper powder has to be used and as the process is a tedious one, the iodine and the sulphur sometimes come out low (see T.1916, *109*, 611)

[†] As these polysulphonium compounds are non-oxylic every element in them admits of its percentage being determined by direct analysis; it has not been however deemed essential to do so in every individual case.

TRINUCLEAR CONDENSATION.

(5) 
$\begin{array}{c}S-(C_2N_2S)_2S_4-S\\ |\qquad\qquad\qquad |\\ Hg-O-Hg\end{array}$
and methyl iodide: formation of Trithiobiozole hexasulphonium methyl mercuri-iodide.



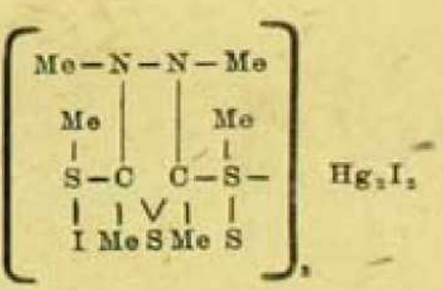
The product on refluxing the parent sulphoxy compound with methyl iodide was an "oil;" it was dissolved in hot acetone, which on cooling deposited a crystalline mass. This on recrystallisation from hot acetone yielded needle shaped crystals m.p. 101-102°, it was in fact the same compound as described on p. 61 (compound No. 1) The original mother liquor on concentration gave two successive crops m.p. 85-86°., the analysis of which is given below.

0·2947 gave 0·0635. Hg = 21·55

0·1480 „ 0·0470 CO_2. C = 8·66

$C_{14}H_{24}N_6S_9Hg_2I_8$ requires Hg = 20·20 ; C = 8·48

(6) *The compound with methyl iodide in which all the double bonds are saturated, viz ;*



The method of preparation and purification was the same as in the case of the preceding compound. It was a white crystalline substance, m. p. 94°.

0·3717 gave 0·3678 Hg and 0·3075 $BaSO_4$. Hg = 18·24 ; S = 11·36
0·2213 „ 0·0882 CO_2 and 0·0506 H_2O. C = 13·15 ; H = 2·54
$C_{24}H_{54}N_6S_9Hg_2I_8$ requires Hg = 18·78 ; S = 13·52 ; C = 13·52 ; H = 2·53

Formation of this type of compound has been noticed only in this one instance.

(7) *The hexasulphonium propyl compound :*

It conforms to the ordinary type (cf. No. 5).

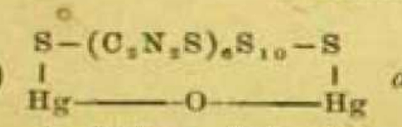
0·2912 gave 0·0540 Hg and 0·2404 AgI. Hg=18·54 ; I=44·61

0·1467 „ 0·0886 CO_2. C=16·47

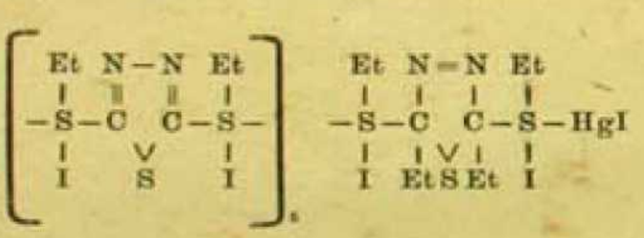
$C_{30}H_{56}N_6S_9Hg_2I_8$ requires Hg=18·14 ; I=46.1 ; C=16·3

As will be noticed, the trinuclear sulphoxy compound gives compounds No. 1 and 5 with methyl iodide ; of course, the latter in major proportion. This tendency towards the formation of the di-nuclear tetrasulphonium compounds from the higher nuclear sulphoxy bodies is particularly noticeable in the case of interaction with ethyl iodide. With this alkyl iodide only the di-nuclear sulphonium compound (No. 2) is always obtained, even from tri-and tetra-nuclear sulphoxy derivatives. In all these cases of formation of a lower member from the higher sulphoxy compounds, a dark brown pasty substance with a penetrating odour and lachrymal properties was always formed, which resisted all attempts at purification.

Hexanuclear Condensation.

(8) 

$\overset{O}{S}-(C_2N_2S)_6S_{10}-S$ over $Hg-O-Hg$ (each S bonded to Hg) and ethyl iodide: *formation of Hexathiobiazole dodecasulphonium ethyl mercuri-iodide.*



It had the m. p. 90-91°

0·3531 gave 0·3269 AgI. I=50·03

0·2008 „ 7 c. c. N_2 at 27° and 760 mm. N=3·90

0·1548 „ 0·0746 CO_2. C=13·14

$C_{40}H_{70}N_{12}S_{18}Hg_2I_{14}$ requires I=51·20 ; N=4·84 C=13·82.

It will thus be seen that the type persists throughout, in that the alteration in the position of the double bond is limited to only one nucleus of the chain.

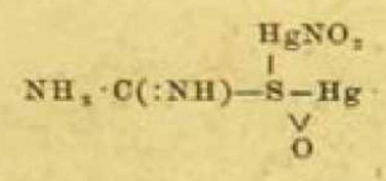
In the previous communications the compounds hitherto described were tentatively classed under the sulphonium group, though no direct proof could be adduced for adopting this view. One of the purest compounds of these series, *viz.* $Me. EtS_2.HgI_2. EtI$; (T. 1916-*109*, 606) was selected for molecular weight determination in acetone solution by the ebullioscopic method; the value obtained was 712, that required by theory being 718. It is thus evident that the constitution is atomic; in fact, Hilditch and Smiles threw out a suggestion in the case of monosulphonium compounds that these are not molecular. (T. 1907, *91*, 1396). A study of the physical properties of the interesting polysulphonium compounds treated of in this paper is being undertaken, which, it is hoped, will throw additional light upon their constitution.

Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides Part VII. Chain Compounds of Sulphur.

By

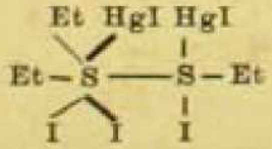
Prafulla Chandra Rây.

The present investigation deals with the chain compounds of hexavalent sulphur. On treating the product of interaction of thiocarbamide with mercuric nitrite, *viz.*, the sulphoxynitrite,



$$NH_2\cdot C(:NH)-\overset{\overset{HgNO_2}{|}}{\underset{\underset{O}{\vee}}{S}}-Hg$$

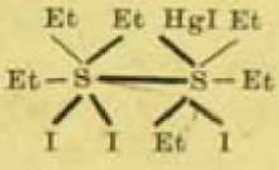
(Trans. 1917, *111,* 102) with ethyl iodide a yellow crystalline substance was obtained. It was found to be completely soluble in acetone. On purification by precipitation with ether it had the m.p. 98—100°. Analysis proved it to conform to the formula $Et_2S_2,EtI,2HgI_2$; in other words, it is a member of the disulphonium series already described (Trans. 1916, *109,* 134) with an additional molecule of mercuric iodide in combination, to which should be assigned the constitutional formula



one of the sulphur atoms in the chain becoming hexavalent. The formation of this compound suggested the possibility of the direct conversion of *all* the members of the series, $RR'S_2$, $R'I$, HgI_2 into $RR'S_2$, $R'I$, $2HgI_2$. This anticipation has been realized with one notable exception. When the alkyl radical happens to be methyl, combination with an extra molecule of mercuric iodide does not take place. The presence of the radical ethyl, on the other hand, favours the combination. Thus in the above series where $R=Me$ and $R'=Pr$ and Bu the extravalencies of the sulphur atom are not revived; but if R' happens to be ethyl, this anomaly disappears. To what extent ethyl favours the increase in valency will be evident from a typical case.

When the ethyl mercaptide nitrite (Et-$SHgNO_2$) is treated with methyl iodide, by an interchange of the radical we get $EtMeS_2$, HgI_2, MeI (l.c. 603); but in this case although there are two methyl groups the presence of a single ethyl radical is sufficient to counteract the prejudicial influence of the former and the compound $EtMeS_2$, MeI, $2HgI_2$ is readily formed.

The marked genetic affinity of the radical ethyl for sulphur and its influence in the increment of its valency is further evidenced by the fact that a compound of the empirical formula Et_4S_2, 2EtI, HgI_2 has also been obtained from ethyl sulphide by its interaction with ethyl iodide and mercuric iodide. On repeating Smiles' experiment (Trans. 1900, 77, 161) under slightly altered conditions, with a view to ascertain the maximum valency of sulphur, it was noticed that while the main product was $(C_2H_5)_3SI$, HgI_2, as found by the above chemist, there was always a considerable amount of a shining crystalline substance, practically insoluble in cold acetone. As it had a sharp m.p. when crystallized out from hot acetone, it was subjected to analysis, which established the formula given above. What evidently happens is that under the joint action of mercuric iodide and ethyl iodide or rather their ions, the divalent sulphur atoms of two adjacent molecules of ethyl sulphide become hexavalent, by their dormant valencies becoming active and they coalesce into a single molecule thus :



It is remarkable that in the above reaction if ethyl iodide be substituted for methyl, propyl, or butyl iodide the products formed in each individual case is found to be completely soluble in acetone and conforms to the general formula $Et_2RISHgI_2$, but no product of the fusion of two ethyl sulphide molecules is formed. The differential property of ethyl as contradistinguished from other alkyl radicles is thus brought into relief.

It was expected that the general method of the preparation of the disulphonium compounds already described, *viz.* the treatment of ethyl mercurimercaptite nitrite $EtSHgNO_2$ with ethyl iodide should also yield the chain compound with both the sulphur atoms as hexavalent. This expectation has also been fulfilled. The latter compound is formed in such a small quantity that on previous occasions its formation was overlooked. It has already been shown that ethyl disulphide, ethyl iodide and mercuric iodide also combine directly to yield the disulphonium compound, Et_2S_2, HgI_2, EtI. (l.c.). Recently this preparation has been repeated and it has been found that the hexavalent *di*sulphur compound is also formed in considerable quantity along with the former. It is thus evident that both the tetra-as also the hexavalent chain compound of sulphur is formed simultaneously.

It is of interest to note that Smiles and Hilditch who treated an acetone solution of equimolecular proportions of ethyl disulphide and mercuric iodide with ethyl iodide obtained *diethyl thioethyl sulphonium dimercuric sulphide.* $(C_2H_5)_3S_2I$, $2HgI_2$ (Trans. 1907, *91*, 1396). It is evidently the same compound as has been described above.

An explanation may be offered as to why it is that in the first series of compounds only one of the two atoms of sulphur can behave as hexavalent; here the tetravalent sulphur being already weighted with the heavy load of the ions of HgI′ and I′ has lost the capacity to take up additional charge; in other words, to acquire the maximum valency. In the solitary instance, however, in which both the sulphur atoms happen to be hexavalent it will be noticed that there is only one set of HgI′ and I′ions; the sulphur atom which have these latter has got attached to it three additional comparatively light Et radicals, whereas, the other sulphur atom not having to bear the load of the heavy HgI′ is in a position to take up three Et's and two I's. Facts are already known which go to support the view that the maximum valency of an element is often conditional upon the load of the radicles. The author has in a previous communication shown that platinum when attached to the radical of phenyl dithiobiazolinesulphydrate behaves as trivalent. It is none the less inexplicable why the light radical methyl should stand in the way of one of the atoms of sulphur attaining its maximum valency. The anomalous behaviour of the first member of the alkyl series is, however, well known.

EXPERIMENTAL.

General method of Preparation of the series R_2S_2, RI, $2HgI_2$ has already been incidentally described. These members are readily obtained by dissolving the corresponding disulphonium compound in acetone and adding mercuric iodide to the solution till no more is taken up. The thick golden yellow liquid is decanted off the undissolved iodide. On adding ether to its acetone solution a copious deposit of yellow mealy crystals is obtained. Solution in acetone and precipitation by ether is repeated till the product gives a fairly sharp melting point. It has been found that in some instances as specially in the case of methyl sulphonium compound, Me_2S_2, MeI, HgI_2, the acetone solution at first takes up a considerable quantity of mercuric iodide but purification by the above process gradually removes all the mechanically held mercuric iodide, which evidently remains obstinately adhering to it.

Result of Analysis.

(1) (*a*) From the sulphoxy nitrite derivative of thiocarbamide: m. p. 98°

0·3656 gave 0·1250 Hg, 0·3540 AgI and 0·1029 $BaSO_4$. Hg=34·19; I=52·32; S=5·50

0·2442 gave 0·0570 CO_2 and 0·0356 H_2O. C=6·37; H=1·62

Calc. for Et_2S_2, EtI, 2HgI_2, Hg=33·73; I=53·54; S=5·4; C=6·07; H=1·26.

(*b*) Direct synthesis *i.e.*, by the direct union of HgI_2 with Et_2S_2 EtI, HgI_2: m. p. 100—101°

0·2118 gave 0·0711 Hg. Hg=33·57

0·2118 gave 0·0532 CO_2 and 0·0352 H_2O. C=6·85; H=1·71.

(2) $MeEtS_2$, EtI, 2HgI_2: m. p. 38—40°

0·2094 gave 0·0452 CO_2 and 0·0466 H_2O. C=5·87; H=2·47

0·3840 gave 0·1236 Hg and 0·3768 AgI. Hg=32·19; I=53·03

Calc. C=5·12; H=1·11; Hg=34·14; I=54·19.

(3) $EtMeS_2$, MeI, 2HgI_2 m. p. 50—55° (not sharp)

0·2467 gave 0·2483 AgI and 0·0840 Hg. Hg=34·05; I=54·39

0·1428 gave 0·0286 CO_2 and 0·0211 H_2O. C=5·46; H=1·64

Calc. Hg=34·55; I=54·84; C=4·14; H=0·95.

(4) $EtPrS_2$, PrI, $2HgI_2+CH_3COCH_3$. This compound contains one molecular proportion of acetone: m. p. 30-31°

0·4410 gave 0·1400 Hg. Hg=31·75

0·1629 gave 0·0586 CO_2 and 0·0352 H_2O. C=9·81; H=1·97.

(5) $EtBuS_2$, BuI, $2HgI_2+1\frac{1}{2}\ CH_3COCH_3$. The substance had the consistency of treacle and had $1\frac{1}{2}$ mols. of acetone combined with it.

0·1340 gave 0·0649 CO_2 and 0·0363 H_2O. C=13·21 ; H=3·01
0·3879 gave 0·1153 Hg and 0·3272 AgI. Hg=29·72 ; I=45·58
Calc. C=13·10 ; H=2·41 ; Hg=30·10 ; 1=47·79.

(6) The compound containing both the sulphur atoms as hexavalent: it was very sparingly soluble in cold acetone but fairly soluble in the boiling solvent, m. p. 146—147°

Prepared from Et_2S :

0·1930 gave 0·1068 CO_2 and 0·0538 H_2O. C=15·09 ; H=3·09
0·2991 gave 0·063 Hg and 0·2916 AgI. Hg=21·06 ; I=52·69
0·4032 gave 0·8400 Hg and 0·2042 $BaSO_4$. Hg=20·86 ; S=6·96
Calc. for $Et_6S_2HgI_4$ C=15·22; H=3·17; Hg=21·14; I=53·70; S=6·77.